





# Dredged Material Research Program



**TECHNICAL REPORT D-78-49** 

# LONG-TERM RELEASE OF CONTAMINANTS FROM DREDGED MATERIAL

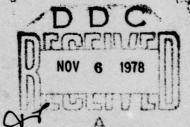
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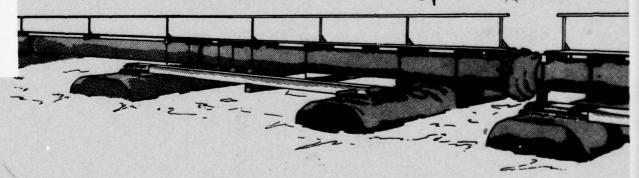
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August 1978 Final Report

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Prepared for Office, Chief of Engineers, U. S. Army Washington, D. C. 20314

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- 1. The Dredged Material Research Program (DMRP) was a broad, multifaceted investigation of the environmental impacts of dredged material disposal that included the development of new or improved alternatives. In the early stages of the DMRP, it became apparent that an understanding of the actual pollution potential of dredging and discharging sediments required substantial state-of-the-art improvement in a number of fundamental biochemical areas. The basic analytical procedure specified in Public Laws 92-500 and 92-532 for use in predicting the water column pollutional impacts of the aquatic disposal of dredged material is referred to as the standard elutriate test. Particularly critical are assessments of the long-term leaching of chemical contaminants from the deposited dredged material to the overlying water column by the readily mobile and bioavailable fraction of dredged material, which may be evaluated chemically by the standard elutriate test or some other sediment chemical analysis. A knowledge of these effects would further support the use of chemical tests as meaningful regulatory tools.
- 2. While developing and initiating the several-year-long program of relevant research, it was found that existing and proposed regulatory guidelines and criteria for dredged material discharges did not include techniques that adequately reflected an effective and implementable procedure for assessing potential environmental impact. Provided an opportunity to help direct the criteria development for the recently promulgated regulatory programs, the DMRP initiated research to develop biological as well as chemical evaluative procedures to assess the bioavailability and mobility of constituents from contaminated dredged material and project their effects on the ecosystem. Essential to this assessment is a knowledge of long-term effects.
- The technical report transmitted herewith represents the results of an 8-month aerobic leaching study to investigate the magnitude and predictability of long-term releases of chemical constituents from dredged material. The study is one of several work units that were included

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under Task 1E (Pollution Status of Dredged Material) of the DMRP; in the DMRP's management structure, it was included as part of the Environmental Impact and Criteria Development Project.

- 4. This report discusses the use of sediment/water column simulations in the laboratory with a large number of sediments (32) representing a broad geographical and pollutional variation and selected from marine, estuarine, and freshwater areas to assess their long-term release of contaminants. The sediment/water systems were studied under aerobic quiescent and mixed conditions. Various sediment chemical analyses, which included the elutriate test and bulk sediment analysis, were conducted to identify and evaluate relationships between sediment chemical characteristics and the long-term leaching of chemical constituents.
- 5. Results of the long-term leaching investigation demonstrated that under the aerobic chemical conditions likely to prevail at aquatic disposal sites, total organic carbon, orthophosphate-P, and zinc exhibited the most consistent net releases to the water column. Very little net mass release of mercury, lead, cadmium, or arsenic into the water column was observed regardless of the composition of the sediments. Worst-case evaluation of the potential effects of contaminant releases, conducted by comparing results of this study with the most stringent water quality criteria available, indicated that sediments used in this study would not be expected to cause significant long-term water quality problems. The elutriate test (modified for aeration) and interstitial water analyses demonstrated considerable utility as predictors of potential long-term net mass release of contaminants from sediments.
- 6. The information and data published in this report are contributions to the further understanding of the complex nature of sediment, water, and chemical/biological interactions, and the report establishes a baseline from which to develop meaningful regulatory criteria. It is expected that the methodology employed in this study and the resultant interpretation of the biochemical interactions will be of significant value to those persons concerned with dredged material permit programs.

JOHN L. CANNON

Colonel, Corps of Engineers Commander and Director

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20. ABSTRACT (Continued).

dredged material, an 8-month aerobic leaching study was conducted in the laboratory. A large number of sediments (32) representing broad geographical and pollutional variation were used to ensure wide applicability of study results.

Under the aerobic chemical conditions likely to prevail at aquatic disposal sites, total organic carbon, orthophosphate-P, and zinc exhibited the most consistent net releases to the water column. Very little net mass release of mercury (Hg), lead (Pb), cadmium (Cd), or arsenic (As) into the water column was observed regardless of the composition of the sediments. Worst case evaluation of the potential effects of contaminant releases, conducted by comparing results of this study with the most stringent water quality criteria available, indicated that sediments used in this study would not be expected to cause significant long-term water quality problems.

The Elutriate Test procedure (modified for aeration) and interstitial water analyses demonstrated considerable utility as predictors of potential long-term net mass releases of contaminants from sediments. The Elutriate Test was related to long-term net mass release of copper (Cu), total organic carbon, phosphorus (P), As, Cd, Pb, and Hg after 4 months. Interstitial water analyses were related to net mass release of zinc (Zn), As, Hg, and ammonium-nitrogen (NH4-N) after 4 months of leaching and Hg, total organic carbon, and NH4-N after 8 months of leaching. The ability of the Elutriate Test and interstitial water analyses to predict release decreased slightly as time after initial mixing increased, apparently due to the increased significance of the aquatic chemistry of each constituent.

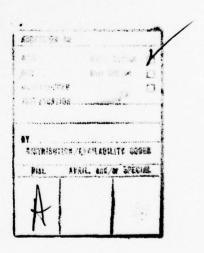
Results from limited sediments incubated under both agitated and quiescent conditions indicated that mechanical agitation did not appreciably enhance long-term net mass release of most constituents. However, one sediment suspension from Oakland Inner Harbor, California, when incubated under aerobic, agitated conditions, exhibited a marked drop in pH from near 8.0 to 3.6. The acidic condition was accompanied by a high net release of trace metals. The same sediment, incubated under aerobic, quiescent conditions did not lower the overlying water pH and did not release significant amounts of trace metals. If disposed of in an upland and drained disposal site, such a sediment could oxidize, become acidic, and pose a potentially severe environmental problem.

Manganese (Mn) and NH<sub>4</sub>-N exerted no long-term effects on water quality. Large amounts of Mn and NH<sub>4</sub>-N were released during the Elutriate Test and presumably when the leaching columns were prepared. However, at the end of a 4-month incubation both constituents were usually present in lower concentrations than in the initial disposal site waters. These results indicate that Mn and NH<sub> $\Lambda$ </sub>-N were being actively removed from the water column.

Consideration of net mass release during the Elutriate Test procedure and other short-term extractants can provide useful information on the probable direction (i.e., sediment to water, to sediment) of long-term net mass release when concern exists over possible contaminant releases at aquatic disposal sites. However, because the relationships are based on laboratory observations and have not been field verified, caution in their use is recommended.

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#### PREFACE

This report presents the results of a study conducted to examine the magnitude and predictability of long-term, aerobic, contaminant releases from dredged material. The investigation was conducted as part of the Corps of Engineers Dredged Material Research Program (DMRP), under DMRP Work Unit No. 1E07 entitled "Long-Term Release of Contaminants from Dredged Material," Environmental Impacts and Criteria Development Project (EICDP).

The work was conducted during the period December 1975 - September 1977 by the Environmental Laboratory (EL), U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi. The investigation was conducted by Messrs. J. M. Brannon and I. Smith, and Dr. R. H. Plumb, Jr., Ecosystem Research and Simulation Division (ERSD), EL. The study was under the general supervision of Dr. R. L. Eley, Chief, ERSD, and Dr. John Harrison, Chief, EL. Dr. R. M. Engler served as Project Manager for the EICDY.

The authors would like to express their appreciation to the many people here at WES, the Wisconsin Department of Natural Resources, New York Department of Environmental Conservation, the Universities of Connecticut, Georgia, and Oregon, and the Norfolk and San Francisco Districts, who obtained the samples used in this study.

Directors of WES during the conduct of this study and preparation of this report were COL G. H. Hilt, CE, and COL J. L. Cannon, CE. Technical Director was Mr. F. R. Brown.

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# LONG-TERM RELEASE OF CONTAMINANTS FROM DREDGED MATERIAL

#### PART I: INTRODUCTION

- 1. Man's activities have increased the loading of municipal and industrial contaminants to the nation's waterways. One result of this loading has been to increase the concentration of many contaminants in sediments, thus generating concern that dredging and aquatic disposal of such sediments may adversely affect water quality and aquatic organisms. Concern about sediment contamination is amplified by the fact that the U. S. Army Corps of Engineers has dredged an average of 290 million cu m annually, approximately half of which has been disposed of at open-water sites. 1
- 2. Prior to 1975, there was no unified approach to assess the potential environmental effects of a proposed dredged material disposal operation. This void was filled with the passage of the Federal Water Pollution Control Act Amendments (Public Law 92-500) in 1972 and the promulgation of interim technical guidance for Section 404(b) of the Act in 1975. The interim guidance specified chemical analysis, bioassay, and mixing zone assessment procedures that could be used in the environmental evaluation. <sup>2</sup>
- 3. One of the justifications for this study resulted from concerns expressed during the development of the Interim Guidance for Ecological Evaluations of Dredged Material Disposal. The only chemical tests considered during the development period were a total sediment analysis and the Elutriate Test. The total sediment analysis, or bulk analysis, was used to characterize the dredged material and for site comparisons. The Elitriate Test was used to indicate potential water quality impacts since was reasoned that chemical contaminants would have to be release to the water column in order for adverse impacts to occur. However, this approach was criticized because the Elutriate Test is of a 30-min duration, whereas disposed sediments would be in contact with overlying water for a longer period of time.

- 4. It is impractical to suggest a long-term (of many months) study for use as a routine regulatory tool, but the information gained from a long-term leaching study could be helpful in applying the results obtained using the procedures specified in the inland disposal interim guidance and the implementation manual for evaluation of environmental effects of dredged material discharge in ocean waters. $^3$ Quantification of long-term net mass release of contaminants associated with dredged ediments into the overlying water is a difficult field problem. Contaminant inputs into the disposal site water column from sources other than deposited dredged material may effectively mask contaminant release from the dredged material. Also, at most open-water disposal sites, natural variation of contaminant concentrations in the water column and rapid dilution of released contaminant concentrations further handicap field assessment of long-term contaminant release patterns. A consideration of the difficulties mentioned previously and the logistics of initiating a field sampling program to determine the effect of contaminants associated with dredged material on the overlying water led to this laboratory study.
- 5. The purpose of this investigation was to observe the release of chemical contaminants from a wide variety of dredged sediments and to determine possible relationships between long-term net mass release and short-term chemical characterizations of the same sediments. The leaching was conducted with water obtained near each collection site and under chemical conditions similar to those found at aquatic disposal field sites. This report presents (a) results of long-term aerobic leaching and the net mass release of contaminants associated with dredged material to the overlying water and (b) an examination of the relationship between long-term mass release and contaminant release from the same dredged sediments in the Elutriate Test and other short-term chemical leaches.

#### PART II: REVIEW OF LITERATURE

- 6. The potential environmental effects of the open-water disposal of dredged material have been receiving increased attention. Concern about the potential adverse effects of dredged material disposal on water quality is due to the large quantity of sediments dredged annually and the high concentration of chemical constituents associated with some of these sediments. Water quality changes that may occur as a result of dredged material disposal can be categorized as being primarily (a) physical effects or (b) chemical-biological interactive effects. While the physical effects can result from the presence of dredged material, dredged material must interact with the disposal site water in order to cause chemical-biological effects. The interaction must result in constituent migration from the dredged material.
- 7. Sediment constituent mobility is the result of many factors. The degree of dredged material-water interaction and the conditions under which it occurs will determine to a great extent whether constituents will migrate from the dredged material into the water, be adsorbed from the water onto the dredged material, or be released into the water only to be quickly precipitated or readsorbed by the dredged material as its chemical properties are altered. Thus, even though dredged material may be grossly contaminated, the conditions which favor interaction between water and dredged material may be such as to preclude significant movement of contaminants into the water column.

#### Factors Affecting Sediment-Water Interactions

8. Mobility, or migration of chemical constituents from dredged material, is essential if dredged material is to have an effect on the water column. Lee and Plumb<sup>4</sup> have identified nine factors that could influence constituent release from dredged materials: dissolved oxygen concentration, agitation, time of contact, characteristics of water, solid-liquid ratio, Ph, particle size, handling of solids, and solid-liquid separation. Other literature reviews<sup>4,5</sup> have also cited many of

these factors as being important in regulating the release of chemical constituents from sediments and/or dredged material. This review will consider only those major factors that could affect the net mass release of contaminants under the experimental conditions used in this study.

#### Oxygen status of the water

- 9. The flux of many elements from sediments into the water column has been shown to be greatly dependent upon the concentration of oxygen in the overlying water. Mortimer<sup>6,7</sup> concluded that chemical exchange from sediment to the overlying water may exert a measurable but quantitatively unimportant influence upon chemical concentrations of materials in overlying waters as long as oxygen concentrations at the sediment interface remained above 1 to 2 mg/ $\ell$ . Fillos and Molof showed that the release of phosphate and ammonia from benthic deposits increased appreciably when dissolved oxygen concentrations in the overlying water fell below 1.5 mg/ $\ell$ . They attributed the increase in the release rate of phosphorus to two factors: (a) the response of bacteria to low oxygen levels and (b) destruction of the adsorptive capacity of the mud surface under reducing conditions. Chen et al. investigated the migration of trace metals between the interface of sea water and contaminated surficial sediments. The amount of iron (Fe) and Mn released from the sediment during a 5-month leaching period was greater when the water column was anoxic. The amount of nickel (Ni), Cd, Cu, Pb, and Zn released was greater when the overlying water was aerobic. Chen et al. concluded that the type of sediment did not control the direction of trace-metal migration. The direction of trace-metal migration was controlled mainly by the chemistry of the immediate overlying water as well as that of the interstitial water, the principal chemical factors being the levels of dissolved oxygen and sulfides.
- 10. The studies presented previously have examined the role of oxygen in regulating contaminant release from quiescent sediment-water systems. It is reasonable to expect that dissolved oxygen concentrations would also affect contaminant release patterns from agitated sediments and dredged material. Lee et al. 10 evaluated the operating

parameters that could affect Elutriate Test (short-term agitated leach of dredged material with water) results and found Elutriate Test tracemetal results to be most sensitive to the oxygen content of the disposal water. The data of O'Connor<sup>11</sup> also indicated that Elutriate Test tracemetal results depended upon the oxygen status of the site water during the test. Oxygenated water resulted in the formation of iron oxides that adsorbed trace metals. Brannon et al.<sup>12</sup> found that the concentrations of orthophosphate released into site waters during the Elutriate Test procedure were inversely related to the concentrations of interstitial water and ammonium-acetate-extractable ferrous iron in the sediment. This suggests that orthophosphate was removed from solution as a consequence of ferrous iron oxidation and precipitation during the test procedure.

- 11. In another leaching study, Lopez 13 found high Cu concentrations in the waters of Torch Lake, Michigan, ranging from 25 to 100  $\mu g/\ell$ . The sediment in this lake was derived primarily from mine tailings that contained from 0.13 to 0.38 percent Cu. Lopez 13 observed a greater release of Cu under aerobic conditions from these sediments rather than anaerobic conditions. Gambrell et al. 14 has also found that release of Cu to the water-soluble phase in sediment-water slurries was favored under oxidizing conditions. Austin and Lee 15 studied the longterm release of nitrogen compounds from Lake Mendota and Trout Lake sediments under both aerobic and anaerobic conditions. They found that the concentration of dissolved oxygen was probably the most important chemical parameter affecting the amount and species of nitrogen compounds released from a sediment. The amount of dissolved inorganic nitrogen released from the sediments under aerobic conditions was from 2.3 to 7 times greater than the amount released from the same sediment under anaerobic sediments.
- 12. The studies reviewed in this section have shown that the oxygen status of the leaching water is one of the most important parameters controlling contaminant release from sediments. In general, the oxidized forms of Fe and Mn are less mobile and have lower solubilities than the reduced forms. The compounds of Cd, Cu, Zn, Pb, and

Ni present under oxygenated conditions are more soluble than their respective compounds, such as sulfides, present under anaerobic conditions. Orthophosphate (0-PO<sub>4</sub>) and ammonium-nitrogen (NH<sub>4</sub>-N) are released in greater quantities under anaerobic conditions, but a larger amount of nitrogen is released under aerobic conditions.

# <u>Sediment-water exchange under</u> quiescent and agitated conditions

- 13. The degree of agitation under which a sediment-water mixture is incubated can affect the rate and magnitude of mass release. Sediment-water systems that are completely mixed are controlled by the exchange reaction between sediment and water rather than the hydrodynamics of the system, as is the case with leaching under quiescent conditions. Lee considered that leaching conducted under quiescent conditions may represent somewhat less than the actual amounts of exchange that would occur in the natural environment. However, completely mixed systems may overestimate release in the natural environment because the same degree of mixing in the laboratory and in the natural environment is rarely achieved. It is therefore virtually impossible to exactly simulate the quality and quantity of field mixing in the laboratory. However, by proper choice of experimental conditions, it may be possible to identify the dredged material and water properties that inhibit or stimulate the release of contaminants into water.
- sediments to water under agitated and quiescent conditions have been explored by a number of workers. Lee<sup>5</sup> compared the work of Austin, <sup>16</sup> who leached Lake Mendota sediments under aerobic, mixed conditions, and Sawyer et al., <sup>17</sup> who leached Lake Mendota sediments under aerobic, quiescent conditions. Lee<sup>5</sup> reported that nitrogen release was 50 times greater when the sediments were mixed during incubation. Plumb has extensively investigated the release of chemical constituents from taconite tailings and Lake Superior sediments into Lake Superior water under quiescent and agitated aerobic conditions. He found that the release patterns observed were dependent upon the constituent under

consideration. The greatest cumulative conductance release was observed from tailings and Lake Superior sediments leached under agitated conditions. Calcium (Ca) release was found to be essentially the same for taconite tailings incubated under agitated and quiescent conditions, although the rate of release was faster in the stirred tailings suspensions. Magnesium (Mg) release, however, was diminished under quiescent conditions. Plumb $^{18}$  has also found a greater initial release of Cu and Zn from taconite tailings leached under quiescent conditions. Over time, Cu and Zn concentrations then decreased in both the quiescent and stirred containers, although the decrease was slower in the quiescent containers. This release pattern for Cu and Zn was attributed to the slower release of dissolved solids under quiescent conditions that resulted in a slower increase of solution pH, favoring the solubilization of Cu and Zn in the quiescent containers. Manganese was released under both agitated and quiescent conditions, although the magnitude of release was greater under agitated conditions. Other parameters such as Cd, Pb, and Fe did not demonstrate release patterns that were affected by agitation.

15. An inspection of the results of Plumb 18 revealed that although the magnitude and rate of release under stirred and quiescent conditions differed, the release patterns were similar, with the possible exception of silica. The similarity in release patterns achieved under agitated and quiescent conditions suggests that net mass release patterns under agitated and quiescent leaching conditions will be similar. Also, although it may be impossible to duplicate mixing under field conditions, especially the mixing of sediments by benthic organisms, the factors affecting chemical release trends in the laboratory will in all probability affect chemical release trends in the natural environment.

# Time of contact

16. The short-term interaction of water and dredged material has been extensively studied in both the laboratory and the field.  $^9,10,12,19$  In general, these studies have shown that NH $_4$ -N and Mn are released from sediments in significant quantities. Very few long-term studies on the

release of contaminants from dredged material to water have been conducted.

17. The effect of time of contact on constituent migration from the solid phase to the liquid phase was observed by  $Plumb^{18}$  during a three-year leaching study with taconite tailings. Release patterns varied for each constituent but generally fell into one of four categories. Constituents considered highly soluble (Ca, Mg, alkalinity, total dissolved solids) demonstrated a high initial release followed by an asymptotic leveling off. Some constituents (Cu, Zn) demonstrated an initial release followed by an eventual loss from solution while others (Pb, Cd) showed no release during the 1000-day period. Finally, silica demonstrated a step-function release pattern suggesting that release was dependent upon a hydrolysis process or some other chemical reaction. These release patterns are not exhaustive (i.e., a constituent could show a net loss with time) and are not unique to taconite tailings. Chen et al. observed similar release patterns in a 150-day quiescent leaching study with dredged material and seawater. The data of Chen et al. revealed that under oxidizing conditions most metals and nutrients studies had achieved fairly stable concentrations near the end of a 150day incubation period. Plumb 18 found that cumulative conductance release from Lake Superior sediments under aerobic, quiescent conditions had leveled out after 100-200 days of contact time. The data of Plumb $^{18}$ also indicated that the majority of aerobic, quiescent leachates of taconite tailings and Lake Superior sediments had achieved fairly stable concentrations of Fe, Cu, Zn, Cd, and Pb in Lake Superior water within 100-200 days. The results of the studies presented above indicate that for most substances, a 150-day or longer laboratory leaching period under aerobic, quiescent conditions should be sufficient to ensure that fairly stable, steady-state contaminant concentrations will be achieved in the overlying water.

### Salinity

18. When dredged material is disposed of in saline disposal areas, the salinity of the disposal site water may increase the magnitude of contaminant release during and after disposal. Lee et al.  $^{10}$  has

attributed the effect of salinity and salinity changes on sorption-desorption to ion exchange, alteration of clay crystal structure, or flocculation of organic matter and clay particles. Serne and Mercer 19 found that under oxidized agitated conditions, dredged material from San Fransciso Bay released significantly greater amounts of Zn, Cd, and for one sediment, Cu as the water salinity increased.

- 19. It has been shown that metals associated with particulate matter in rivers may desorb when encountering salt water. DeGroot and Allersma<sup>20</sup> and DeGroot et al.<sup>21</sup> have reported that metals remain fixed to the suspended matter in the Rhine delta until influenced by the sea. Metals are then solubilized partly as organometallic complexes, although inorganic ions such as the chloride anion (C1 ) can play a role in the mobilization process. Mercury has shown the greatest mobility, followed in decreasing order by Cu, Zn, Pb, chromium (Cr), and As. Mobilization at intermediate levels took place with cobalt (Co) and Fe. The elements lanthanum (La), scandium (Sc), samarium (Sm), and Mn were not shown to be subject to solubilization processes. These mobilization processes were used to explain the less contaminated sediments found in the lower courses of the Rhine delta. 20,21 Muller and Forstner 22 have shown, however, that mixing of highly polluted sediments with relatively unpolluted North Sea sediments, rather than solubilization of sediment contaminants, was the cause of the dilution of heavy metals in the sediments of the Elbe Estuary, which is similar to the Rhine Estuary.
- 20. Mixing of fresh and salt water can apparently cause both precipitation and dissolution of Mn. Windom et al.  $^{23}$  and Graham et al.  $^{24}$  have shown the Mn from rivers apparently precipitated when salt water was encountered. Evans and Cutshall  $^{25}$  found, however, that Mn associated with particulate matter in the Columbia River was released when mixed with seawater.
- 21. As is evident from the previous discussion, no clear picture of the effect of salinity on contaminant mobilization has emerged. It is probable, however, that the effect of salinity and salinity change on trace metal desorption from dredged material will be most pronounced

when dredged material from a freshwater area is disposed of in a saline disposal site. Differences in pH between fresh and saline waters may have an additional effect on sorption-desorption processes. Contaminant desorption tendencies may be counteracted by increasing pH when moving from fresh to saline-water systems as found by Graham et al. In general, solubilization of metals tends to increase with a decrease in pH. 6

#### Other factors

22. The limited discussion of dissolved oxygen, agitation, time of contact, and water characteristics is not meant to imply that other factors such as those identified in literature reviews are not important. Certainly, pH can affect the mobility of sediment-associated constituents and handling of solids can change physical properties that can alter the leaching characteristics of sediments. However, sediments were leached in representative site water with its ambient pH, and no attempt was made to make pH an intentional experimental parameter. Also, every attempt was made to handle all sediments in a similar manner and process them in the same time interval.

# Sediment Constituent Mobility

- 23. A number of studies have been conducted to characterize the capacity of a sediment to release material to the overlying water. Procedures used in these studies have ranged from filtration (to determine interstitial water) to total acid digestion. In addition, several intermediate operationally defined sediment extraction procedures have been used to assess sediment constituent availability. These latter procedures are similar to soil extraction procedures that have been used for many years to define exchangeable, available, and extractable constituents in soil. <sup>26,27</sup>
- 24. The utility of a sediment bulk analysis procedure as an indicator of water quality changes following dredged material disposal was evaluated by Lee and Plumb.<sup>4</sup> It was concluded that such an approach

would be technically unsound because of the implicit and invalid assumption that all forms of the chemical constituents present in the sediment would have an equal impact on the environment. Shapiro et al. 28 concluded that chemical form and solubility are important in determining sediment constituent migration, and Bricker 29 concluded that mobility of sediment associated constituents could not be predicted with bulk analysis results.

- 25. A major reason that bulk analysis procedures have been ineffective in evaluating sediment constituent mobility is that sediment constituents are distributed among several geochemical phases. It has been shown by Brannon et al.,  $^{12}$  Chen et al.,  $^{9}$  and Luoma and Jenne  $^{30,31}$  that this distribution or elemental partitioning of sediment constituents varies for each sediment source and each constituent. It has been suggested that this partitioning will influence the extent of sediment constituent mobility  $^{27}$  and determine the effects of dredged material disposal on water quality.  $^{30,31}$
- 26. No single extract has been shown to be universally successful in defining chemical availability and exchangeability. 32 Consequently, a variety of extraction procedures ranging in severity from distilled water or a dilute salt solution to strong oxidizing agents such as hydrogen peroxide to strong acid solution have been used to define soil or sediment geochemical phases. 26,27 The Elutriate Test, developed jointly by the Corps of Engineers and the U. S. Environmental Protection Agency to evaluate proposed dredged material disposal operations, is similar to the weaker extractants used in elemental partitioning or geochemical phase distribution studies except that disposal site water, rather than distilled water or a well-defined salt solution, is used as the leaching agent. An evaluation of the Elutriate Test 4 indicated that results could be influenced by many factors but that the procedure was potentially useful for assessing the impact of dredged material disposal on water quality. Lee et al. 10 later showed Elutriate Test results to be reproducible, provided dissolved oxygen concentrations and the liquidsolid ratio were carefully controlled during the test.

27. Brannon et al. 12 compared Elutriate Test results for a number of sediments with the results of a variety of short-term extracts of the same sediments. The most frequent statistical correlation in the data was between Elutriate Test results and the interstitial water and exchangeable phase results. Since the interstitial water phase and exchangeable phase of the sediments were considered the most labile, Elutriate Test results were considered to be indicative of the more mobile parameters likely to affect water quality during dredged material disposal operations.

# Long-Term Studies

- 28. Precedents exist for using water extracts to define the mobility of sediment-associated constituents, and Elutriate Test results have been shown to be correlatable with some frequently used geochemical phase extracts. However, the utility of Elutriate Test results to predict long-term constituent release is largely unexplored. In fact, only one example is known where long-term leaching data and Elutriate Test results exist for the same material. Plumb lobserved the leaching of taconite tailings for a 3-year period and Plumb and Lee conducted Elutriate Tests with taconite tailings.
- 29. The calculated solubility (based on specific conductance data) of taconite tailings during long-term leaching studies, ranged from 0.1 to 3.0 percent depending on the solid-liquid ratio, agitation, pH, leachate composition, and pretreatment of tailings. Ninety-five percent of the solids migrating from tailings during the leaching period were accounted for by alkalinity, Ca, Mg, sodium (Na), and Mm. Also, Mm was the only metal released from tailings that exceeded water quality criteria. The largest release during the Elutriate Test relative to initial site water concentrations, occurred with Mm. Another five parameters, potassium (K), silica, Zn, nitrite (NO<sub>2</sub>), and nitrate (NO<sub>3</sub>) increased by at least 20 percent during the Elutriate Test, although the leaching results indicated no water quality problems. Thus, the Elutriate Test satisfactorily assessed potential water quality problems

due to the leaching of taconite tailings.

30. In another comparison of short-term and long-term leaching studies, Li et ai. 33 observed the distribution of exchangeable inorganic phosphate in lake sediments. Long-term suspensions equilibrated as one percent sediment-water mixtures were sampled with time to determine the phosphate distribution. Short-term distribution of added 0-PO<sub>4</sub> after 24 hr incubation in a 1 percent sediment suspension was also measured. Results suggest that the short-term method was suitable for measuring exchangeable phosphate in sediments because of the similar results even though equilibration time, oxidation-reduction potential, and degree of agitation varied. Although the study was not specifically concerned with transfer to the water column, the results suggest that short-term studies can be used to assess long-term changes.

#### PART III: EXPERIMENTAL METHODS

#### Sampling Areas

- Sediment and water samples were collected with the cooperation of personnel at active research and dredging sites selected on the basis of information obtained from the Corps of Engineers Dredged Material Research Program (DMRP). Sampling areas were selected to provide dredged material with a variety of physical and chemical characteristics. A total of 16 areas were sampled, including the DMRP aquatic disposal field study areas at Ashtabula, Ohio; Duwamish Waterway, Washington; Columbia River, Oregon; and Galveston, Texas. The general geographical locations of the sampling areas are shown in Figure 1. Four dredged material samples were taken at each of the Duwamish Waterway, Ashtabula River, and Columbia River sampling areas. Three dredged material samples were taken at the Houston Ship Channel sampling area. Two dredged material samples were taken at each of the Mobile Bay, Branford, Bridgeport, James River, and Oakland Harbor sampling areas. One dredged material sample was taken at each of the remaining sampling areas. A total of 32 separate dredged material samples were obtained.
- 32. Water samples were obtained from dredged material aquatic disposal sites at the Duwamish Waterway, Branford, Bridgeport, Ashtabula River, Houston Ship Channel, and Columbia River sampling areas. Water samples from the remaining areas were taken from areas near the dredged material sampling sites that would be representative of the water (fresh, brackish, saline) in which the material would be disposed.

# Field Sampling Procedures

33. Dredged material samples were taken using grab samplers. Immediately after sampling, the sediment was placed in a  $7.6-\ell$ , widemouth, polyethylene container. The container was completely filled with dredged material, keeping aeration and manipulation to a minimum, then sealed.

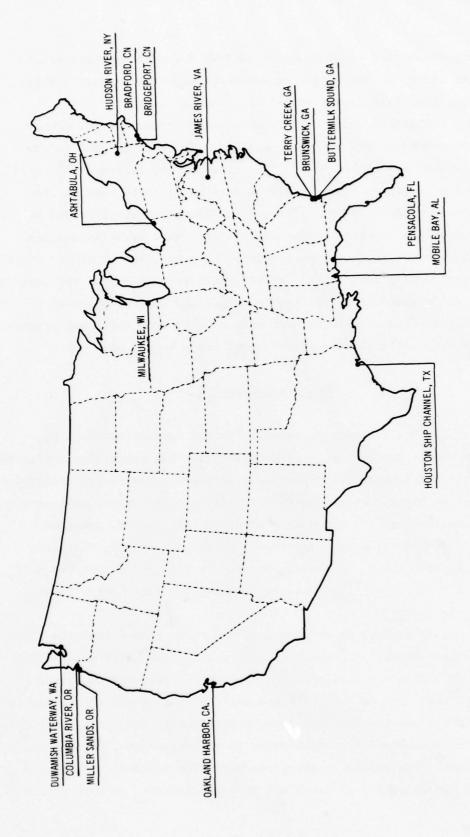


Figure 1. Sediment sampling areas

The dredged material samples were iced down for preservation; transported to the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi; and stored at  $4^{\circ}$ C until used.

34. Unfiltered water samples were taken at each of the sampling areas and stored in polypropylene bottles. Water to be used in the Elutriate Test was packed in ice for transport and stored at 4°C until used in the Elutriate Test. Disposal site water to be used in the leaching experiment was not refrigerated during transport to WES due to the large volume of water needed and the fact that relative changes would be observed in the leaching study. However, the water was stored at 4°C immediately upon arrival at WES until it was used in the leaching study. All containers for dredged material and water samples were thoroughly cleaned with 10 percent hydrochloric acid (HCl) and rinsed 10 times with redistilled, demineralized water before use.

# Short-Term Leaching

- 35. All samples were processed within 7 days after sampling. Prior to sample processing, a disposable glove bag containing a nitrogen atmosphere under positive pressure was prepared. Oxygen-free conditions in the glove bag were verified with a polarographic oxygen analyzer. Sample handling and all steps in the interstitial water, ammonium acetate, and hydroxylamine hydrochloride extractions were conducted under a  $N_2$  atmosphere. All hardware used in the extractions was acid washed in 10 percent HCl and rinsed in distilled water prior to use. Interstitial water
- 36. Each dredged material sample was first placed into the glove bag. Sample consistency permitting, the wet dredged material was then blended with an electrically driven polyethylene stirrer contained in the glove bag. Dense, sandy dredged material that could not be electrically blended was blended manually. Approximately 300 cc of the blended dredged material was then transferred to an oxygen-free, polycarbonate 500-ml centrifuge bottle in the glove bag. The subsample was spun down at 9,000 rpm (13,000 g's) for 5 min in a refrigerated (4°C) centrifuge.

This was sufficient to obtain approximately 40 percent of the total sediment water, except in sandy dredged material (>80 percent sand), where interstitial water could not be obtained by this method. Following centrifugation, the interstitial water was vacuum filtered under nitrogen through a pre-washed 0.45  $\mu m$  pore-size membrane filter and immediately acidified to a pH of 1 with 6  $\underline{N}$  Ultrex HNO $_3$ . A subsample to be used for Hg analysis was further preserved with two drops of a 1 percent aqueous solution of  $\mathrm{KMnO}_4$ .

# Ammonium acetate extraction

- 37. A subsample (approximately 20 g dry weight) of each blended dredged material sample was weighed into an oxygen-free, tared, 250-ml centrifuge tube containing 100 ml deoxygenated 1 N ammonium acetate  $^{27}$  adjusted to a pH of 4.8 with concentrated HNO $_3$ . The ratio of sediment to extractant was approximately 1:5. Other subsamples of the blended dredged material were removed to determine the percent solids. The dredged material suspensions were shaken for 1 hr, centrifuged at 6000 rpm for 5 min, and then vacuum filtered under oxygen-free conditions. The filtrates were acidified to pH 1 with concentrated HNO $_3$  and stored in polyethylene bottles for subsequent analysis. A subsample to be used for Hg analysis was further preserved with two drops of a 1 percent aqueous solution of  $\mathrm{KMnO}_4$ .
- 38. Additional subsamples from the blended dredged material were set aside for determination of total metals, total Kjeldahl nitrogen (TKN), total organic and inorganic carbon, cation exchange capacity (CEC), and particle-size distribution (PSD).

# Hydroxylamine hydrochloride extraction

39. A subsample of the blended dredged material (2 g dry weight) was weighed into an oxygen-free, tared, 250-ml centrifuge tube containing 100 ml of 0.1  $\underline{\text{M}}$  hydroxylamine hydrochloride -0.01  $\underline{\text{M}}$  nitric acid solution. The solid-to-extractant ratio was approximately 1:50. The mixture was mechanically shaken for 30 min, centrifuged at 6000 rpm for 5 min, and filtered through 0.45  $\mu$ m pore-sized membrane filters under oxygen-free conditions. The filtrate was immediately acidified to pH 1 with concentrated HNO3.

#### Elutriate Test

40. The Elutriate Test was conducted incorporating the modification suggested by Lee et al.  $^{10}$  to standardize oxygen content during the test. Blended dredged material and unfiltered water from the sampling area were mixed in a 1:4 volumetric dredged material-to-water ratio at room temperature (22+2°C). The sediment wet weight added to the elutriate mixture was also determined. The mixture was agitated for 30 min with a magnetic stirrer and compressed air. The suspension was then allowed to settle for 1 hr, centrifuged at 6000 rpm for 5 min, and vacuum filtered through pre-washed 0.45  $\mu m$  pore-size membrane filters. The filtrate was divided into three subsamples. One subsample was immediately analyzed for nutrients. The remaining subsamples were acidified to pH 1 with 16  $\underline{N}$  "Ultrex" HNO $_3$ . One subsample was further preserved for Hg analysis with two drops of a 1 percent aqueous solution of  $\text{KMnO}_4$ .

# Diethylenetriaminepentaacetic acid (DTPA) extraction

41. A subsample (approximately 10 g dry weight) of blended dredged material was weighed into a 250-ml polycarbonate centrifuge tube containing 100 ml of a solution of 0.01  $\underline{\text{M}}$  DTPA, 0.2  $\underline{\text{M}}$  triethanolamine, and 0.02 M CaCl $_2$ . The mixture was shaken for 24 hr, centrifuged at 6000 rpm for 5 min, and vacuum filtered through 0.45  $\mu\text{m}$  pore-size membrane filters. The DTPA extract was then stored in polyethylene bottles for subsequent analyses.

#### Total digestion of dredged material

42. The dredged material subsample set aside for total metal analysis was air dried then ground using an agate mortar. A 2-g subsample was then weighed into a Teflon beaker and 25 ml of  $\frac{8N}{3}$  HNO  $\frac{8N}{3}$  added. The mixture was heated on a hot plate for 1 hr at approximately 82°C. The extract was filtered through Whatman No. 5 filters and brought to a constant volume of 50 ml and stored until analyzed.

#### Total mercury

43. A subsample of each blended dredged material was analyzed for total Hg. The analyses were conducted using a Laboratory Data Control U. V. Monitor Model 1235 by the cold-vapor method given in "Methods for

Chemical Analysis of Water and Waste."<sup>37</sup>
Total PCB's

44. Subsamples of blended dredged material from the Duwamish River, James River, and Hudson River sampling sites were analyzed for total PCB's using solvent extraction followed by gas chromatographic analysis.  $^{38}$ 

# Long-Term Leaching

# Experimental setup

- 45. Long-term leaching of dredged material was conducted in 20-%, cylindrical, linear polyethylene containers. Prior to setup, the leaching columns were initially washed with soap and water, rinsed with tap water, filled with 6 N HCl and allowed to stand for 12 hr, then rinsed 10 times with redistilled deionized water. The leaching experiment was conducted in a dark, controlled environment chamber where the temperature was regulated at 22 + 2°C. The design and loading arrangement of an individual leaching column is shown in Figure 2. A total of 32 of these columns were established for quiescent leaching. Three additional columns were established for leaching under agitated conditions. These three columns differed from the one shown in Figure 2 only by the presence of an electrically driven polyethylene stirrer suspended 4 cm from the bottom of the container. One additional unit was established as a reference column consisting of 10 & of distilled deionized water in one of the polyethylene cylinders used as leaching vessels.
- 46. All leaching columns were kept aerated by slowly bubbling air through the water or slurry. As indicated in Figure 2, the air dispersion bulb was positioned in the leaching vessel such that the bubbling action aided mixing of the water column but did not disturb the bottom sediment.
- 47. Leaching columns were prepared each time dredged material and water samples were received at WES. Following the interstitial water, ammonium acetate, and hydroxylamine hydrochloride extractions, a

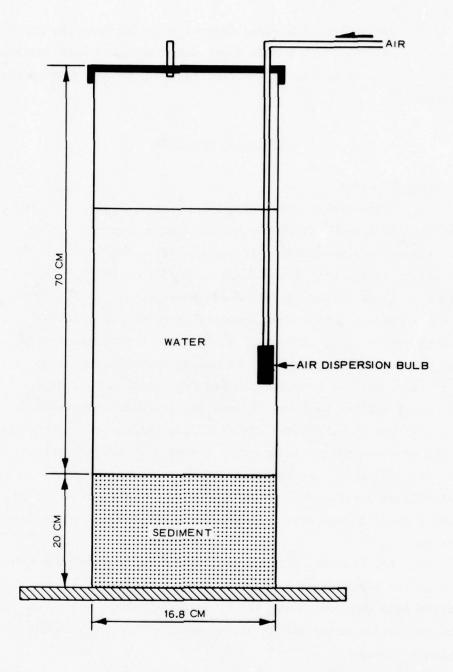


Figure 2. Long-term leaching column setup (figure not drawn to scale)

weighed 4.5-l subsample of the blended, wet dredged material of known moisture content was added to a leaching column. This amount of material was sufficient to ensure that the depth of dredged material in the leaching column would be at least 20 cm. Ten litres of mixed, unfiltered disposal site water was added to the leaching column, and the mixture agitated to simulate worst case disposal operations. Air bubbling was also initiated at this time.

48. Contaminant levels in the disposal site waters were determined in a l- $\mbox{\sc k}$  subsample of the mixed disposal site water to provide leachate background information. The disposal site water was first vacuum filtered through pre-washed 0.45  $\mu m$  pore-size membrane filters. The first 50 ml of filtrate was discarded. The remaining filtrate was apportioned into three separate acid-washed polyethylene bottles. One subsample, for metal analysis, was acidified to pH l with 16  $\underline{N}$  "Ultrex" HNO $_3$ . The second subsample, for nutrient analyses, was initially preserved with one drop of a solution of  ${\rm HgCl}_2$ . The  ${\rm HgCl}_2$  addition was discontinued after it was found that  ${\rm HgCl}_2$  poisoned the catalyst in the Technicon autoanalyzer used for  ${\rm No}_3^-{\rm N}$  analyses. Subsamples for nutrient analyses were not preserved thereafter but analyzed immediately after processing. The remaining subsample for Hg analyses was acidified to pH l with 16  $\underline{\rm N}$  "Ultrex"  ${\rm HNO}_3$  and two drops of a l percent aqueous solution of KMnO $_4$  added.

#### Leachate sampling

49. One-litre leachate samples were withdrawn from the midpoint of the overlying water in the leaching columns at intervals of 120 and 240 days following initiation of leaching. Suspended materials were removed from the sample by vacuum filtration through pre-washed 0.45 µm poresize membrane filters. The first 50 ml of filtrate was discarded. The subsequent filtrate was divided into subsamples and preserved as described for disposal site water in the preceding section. The temperature, pH, DO, and conductance data were obtained immediately on an aliquot of the unfiltered sample. One litre of appropriate disposal site water was added to the original vessels subjected to quiescent leaching conditions. Suspended dredged material removed from the samples

subjected to agitated leaching was replaced in the original leaching vessel along with 1  $\ell$  of appropriate disposal water. These procedures minimized changes in the solid-liquid ratio in each leaching vessel.

50. An additional litre of leachate was taken from quiescent columns where total polychlorinated biphenyls (PCB) were to be determined. The unfiltered sample was immediately placed in hexane-washed glass containers and stored at  $4^{\circ}\text{C}$  until total PCB analyses were conducted.

# Analytical methods

- 51. A combination of three analytical systems were used in all metal determinations. Metal concentrations were first determined using direct flame aspiration with a spectrometrics Spectraspan II ecelle grating argon plasma emission spectrophotometer. For lower concentrations, extracts and leachates were analyzed for Fe, Mn, Zn, Cu, and Pb by the method of standard addition using a Perkin-Elmer Model 2100 heated graphite atomic absorption spectrophotometer. Arsenic and Hg, along with lower concentrations of Cd, were determined with an isotope Zeeman shift atomic absorption spectrophotometer.
- 52. Ammonium-N, nitrate + nitrite -N, orthophosphate, and total phosphate concentrations in extracts and leachate samples were determined using a Technicon Autoanalyzer II. Total organic carbon concentrations in the extracts and leachate samples were determined by dry combustion using a Dohrmann DC 50 Carbon Analyzer.
- 53. Dispersed particle-size distribution  $^{39}$  and cation exchange capacity  $^{27}$  were determined on blended dredged material subsamples from each sampling site. The cation exchange capacity procedure included saturating wet dredged material samples with ammonium, removing excess ammonium with isopropyl alcohol, and extracting the sediments with a series of 2 N solutions of mixed K(1.2N KNO3) and Ca  $(0.8 \text{ N} \text{ Ca}(\text{NO}_3)_2)$  nitrates. Ammonium in the cation exchange extract was determined with a Technicon Autoanalyzer II.
- 54. Total organic carbon was determined by dry combustion. 41
  Inorganic carbon content was determined by treating dried and ground

dredged material with 3  $\frac{N}{42}$  HCl and measuring the decrease in weight resulting from CO  $_2$  loss.  $\overline{^{42}}$ 

52. Total PCB's in the water samples were determined by gas chromatography following solvent extraction.  $^{38}$ 

# Statistical Methods

56. Simple and multivariant linear regression analyses were conducted to determine what relationships, if any, existed between long-term net mass chemical release, and the various sediment and water parameters determined.

#### PART IV: RESULTS

57. Objectives of the study are to examine relationships between the observed long-term mass release from sediments and short-term chemical characterization of the same sediments. Analytical results and responses of individual sediments to specific treatments are identified in the text primarily by site number. This method of identification was chosen for expediency due to the large number of sampling sites utilized during the study and the fact that the behavior of any one particular sediment is irrelevant to the stated study objectives. Site numbers associated with sediment samples from a particular area are presented in Table 1.

#### Sediment Physical and Chemical Characteristics

- 58. Results of sediment physical analyses are presented in Table 2. The sediments exhibited a wide variety of particle size, ranging from nearly pure sand (87 percent sand) in fine samples (Sites 1, 24, 28, 29, 30) to sediments containing 75 percent clay (Sites 15, 16). Sediment cation exchange capacity was equally variable, ranging from 0.3 meq/100 g (Site 24) to 108.5 meg/100 g (Site 23).
- 59. Nitrogen, phosphorus, and carbon analyses for the original sediments are also presented in Table 2. Total Kjeldahl nitrogen varied from 86  $\mu$ g/g (Sites 29, 30, 31) to 3867  $\mu$ g/g (Site 10); total phosphorus varied from 13  $\mu$ g/g (Site 1) to 3900  $\mu$ g/g (Site 26); and total organic carbon ranged from 0.04 percent (Site 31) to 7.3 percent (Site 12). In addition, total (bulk) concentrations for eight metals are presented in Tables 3-10. Except for Hg and As, these data varied by factors of 400 to 5000.
- 60. Each sediment sample was subjected to a modification of the elemental partitioning procedure described by Brannon et al. 12 This procedure consisted of the nonsequential determination of nutrients and trace metal concentrations in the interstitial water, the ammonium acetate extract, the hydroxylamine extract, the DTPA extract, and the

standard elutriate modified for air bubbling. Each extract provides a measure of degree of chemical mobility for contaminants of interest under varying degrees of harshness. For example, the DTPA extraction would be considered a harsher procedure than the ammonium acetate extraction, and the total acid digest mentioned earlier was the harshest extraction procedure used in the study. The concentration of eight metals in each of the short-term extracts is presented in Tables 3-10. The extract compositions were also highly variable and ranged over several orders of magnitude, depending on the source of the sediments and the relative strength of the extraction solvent. A more detailed discussion of the operationally defined sediment fractions is provided by Brannon et al. 12

61. The observed variability in the physical and chemical composition of the sediments used in this study is important for several reasons. First, the data demonstrate the heterogeneous nature of sediments and the variability that can be expected at any one sampling location. Second, and more importantly for this study, the wide range in data provides a more suitable base for statistical treatment of the information, which should improve the reliability of any interparameter relationships that are calculated.

## Long-Term Quiescent Leaching

- 62. A major emphasis of the program was to conduct long-term leaching of the sediment samples in the appropriate site water under controlled conditions. This involved an initial analysis of the site water samples for the 12 parameters listed in Table Al, conductivity, and pH (Table 11). Sediment suspensions were then prepared as outlined in the methodology section and maintained under aerobic, constant temperature (20-22°C) conditions. At elapsed time intervals of 4 months and 8 months, filtered subsamples of each sediment suspension were again analyzed (Tables 3, A2, A3).
- 63. Data from the control column (not presented) indicated that the containers were not a source of contamination. During the sampling

procedure, any solids removed from the long-term leaching subsample by 0.45 µm pore-size filtration were reintroduced into the leaching column with an appropriate quantity of previously unused site water. There were two reasons for this approach. First, it maintained a (relatively) constant solid to liquid ratio during the leaching period. Second, it provided the opportunity to extend the duration of the leaching study at any desired sampling frequency.

64. Prior to subjecting the leaching data to statistical analysis, the movement of chemicals during the leaching period was expressed on a net mass release basis. Net mass release is the change in the mass of chemical constituents in the overlying water compared to the mass originally present in the same volume of site water and was calculated using the method described by Plumb. To calculate the total release of any one constituent, the following approach was used:

On sample day 120:

Total X released = 
$$10(X_{120}) - 10(X_0)$$
,

On sample day 240:

Total X released = 
$$10(X_{240}) + (X_{120}) - 11(X_0)$$

where

X = species of interest
(X) = analytical concentration, mg/l
subscript = sample day

A positive net mass release indicates movement of chemical constituents from the sediment into the overlying water, and a negative value indicates the reverse process.

.65. Evaluation of factors related to chemical constituent concentrations in the long-term leachate was conducted only for the 4-month leachate samples. The water added to bring the leaching containers to volume after the 4-month sampling rendered consideration of any parameter, other than chemical constituent net mass release, invalid for the 8-month leachate samples.

# Copper

66. Total sediment Cu concentrations ranged from 0.33  $\mu$ g/g (Site 1) to 1446  $\mu$ g/g (Site 10) (Table 3). The only less severe extractant that generally mobilized appreciable amounts of Cu (>0.5  $\mu$ g/g) was the DTPA

extractant. By comparison, net mass release of Cu during the Elutriate Test procedure ranged from -0.050 mg (Sites 25, 26, 27) to 0.033 mg (Site 23). Fourteen sediments removed Cu from the site water during the Elutriate Test and 17 sediments released Cu to the site water.

- 67. The calculated net mass release of Cu from each of the sediment/water systems studied is presented in Figure 3. Thirteen sediments released Cu during the 8-month leaching period and nine sediments removed Cu from the site water. Sediments from Site 11 released the greatest amount of Cu, 0.42 mg, or 0.0019 mg/sq cm, over a period of 8 months. Net mass release of Cu during the Elutriate Test procedure was significantly (p < 0.01) correlated with long-term net mass release of Cu in the 4-month leachate ( $r^2 = 0.695$ ) and in the 8-month leachate ( $r^2 = 0.561$ ). Copper concentrations (CCU) in the 4-month leachate were related to DTPA extractable Cu (DCU) and leachate total organic carbon (TOC) concentrations as shown in the following regression equation:
- CCU (4 mos) =  $-0.004 5.96 \times 10^{-5}$  DCU + 0.004 TOC (4 mos)  $R^2 = 0.6744$  Iron
- 68. Total sediment Fe concentrations ranged from  $14 \mu g/g$  (Site 1) to 47,656  $\mu g/g$  (Site 8) (Table 4). Each of the extracts in the elemental partitioning procedure also removed appreciable quantities of iron. This is supported by the fact that each extract exceeded 1000  $\mu g/g$  for 17 of the 32 sediment samples. Mass release of Fe during the Elutriate Test procedure ranged from -0.01 mg (Site 7) to 4.14 mg (Site 2). Twenty-five of 28 sediment samples released Fe during the Elutriate Test. By comparison, only 14 sediment samples produced a net long-term release after 8 months of leaching (Figure 3).
- 69. Long-term net mass release of Fe (RFE) was significantly (p < 0.05) correlated with the 4-month leachate conductivity ( $r^2 = 0.283$ ). Long-term net mass release of Fe in the 8-month leachate was related to total sediment Fe (TFE) and leachate pH (WPH), as shown in the following regression equation:

RFE (8 mos) = 
$$-9.153 - 2.5 \times 10^{-5}$$
 TFE + 1.27 WPH (8 mos)  $R^2 = 0.6507$ 

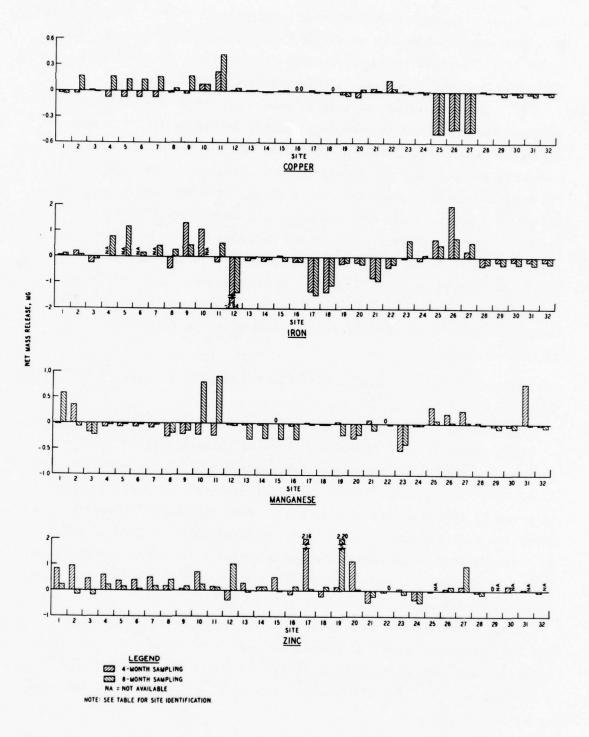


Figure 3. Net mass release of Cu, Fe, Mn, and Zn under quiescent aerobic conditions

Iron concentrations (CFE) in the 4-month leachate (Table Al) were related to ammonium acetate (EFE) and DTPA extractable (DFE) Fe as shown below:

CFE (4 mos) =  $0.026 - 1.63 \times 10^{-5}$  EFE +  $1.99 \times 10^{-5}$  DFE  $R^2 = 0.4558$  Manganese

70. The distribution of Mn in each of the short-term extractants is given in Table 5. An interesting aspect of the data is the general presence of Mn in the potentially more mobile sediment phases. The ammonium acetate phase reached a maximum concentration of 676  $\mu$ g/g (Site 25) and the interstitial water concentration reached a maximum of 30 mg/ $\ell$  (Site 3). The presence of Mn in the potentially more available or mobile phases is also reflected by the fact that the net mass release of Mn during the Elutriate Test procedure was higher than any other metal including a maximum release of 23.54 mg from Site 25 sediments.

71. The net long-term mass release of Mn during the leaching procedure was negative for 26 of the 32 sediment samples. That is, there was a movement of Mn from the original site water to the sediments (Figure 3). Since most sediments had a positive mass release of Mn during the Elutriate Test but a negative release during the long-term leaching procedure, long-term release was not correlated with Elutriate Test results. However, two mathematical expressions were calculated. The 4-month long-term net mass release of Mn (RMN) was related to DTPA extractable Mn (DMN) and hydroxylamine hydrochloride extractable Mn (HMN) as expressed in the following regression equation:

RMN (4 mos) = 
$$-0.084 + 0.001$$
 DMN  $-0.001$  HMN  $R^2 = 0.5549$ 

Manganese concentrations (CMN) in the 4-month leachates were related to DTPA extractable Mn and total sediment Mn (TMN):

CMN 
$$(4 \text{ mos}) = -0.068 + 9.97 \times 10^{-5} \text{ DMN} - 3.03 \times 10^{-5} \text{ TMN}$$
  $R^2 = 0.662$ 

No statistically significant relationships were found for the  $8\text{-}\mathrm{month}$  long-term mass release of  $\mathrm{Mn}$ .

#### Zinc

72. Total sediment Zn concentrations ranged from 1.6  $\mu g/g$  (Site 1) to 1505  $\mu g/g$  (Site 11). Concentrations of interstitial water

extractable Zn and ammonium acetate extractable Zn ranged from 0.001  $\mu g/g$  (Site 25) to 0.66  $\mu g/g$  (Site 18) and from 0.2  $\mu g/g$  (Site 1) to 31.6  $\mu g/g$  (Site 11), respectively. Slightly higher Zn concentrations, ranging from 0.5  $\mu g/g$  (Site 1) to 141.1  $\mu g/g$  (Site 8), were found in the DTPA extractable phase (Table 6).

73. Eighteen sediments produced a net release of Zn during the 8-month leaching period and only seven sediments removed Zn from the water column. The long-term net mass release of Zn ranged from a high of +2.2 mg (+0.01 mg/sq cm) with Site 19 sediments to a low of 0.52 mg (0.002 mg/sq cm) with Site 24 sediments (Figure 3). An analysis of the data indicated one relationship between the 4-month net mass release of Zn (RZN), ammonium acetate extractable Zn (EZN) and interstitial water Zn (IZN):

RZN (4 mos) = 
$$-0.043 + 0.077$$
 EZN  $- 1.291$  IZN  $R^2 = 0.703$ 

Zinc concentrations in the 4-month leachate were also significantly (p < 0.01) correlated with zinc concentrations in the ammonium acetate extract ( $r^2 = 0.603$ ). However, no statistically significant relationships were found between the long-term net mass release of Zn after 8 months of leaching and any of the chemical or physical parameters measured.

### Arsenic

- 74. The distribution of As in each of the sediment extracts is shown in Table 7. The maximum total As concentration reached 9.14  $\mu g/g$  (Site 8) and only on six occasions did any one sediment fraction account for more than 20 percent of the total concentration. During the elutriate testing procedures, only four sediment samples released As to the water phase. These sediments were from Sites 14, 17, 21, and 24 with a maximum release of 0.028 mg from Site 14 sediments. The maximum loss of As to the sediments during elutriate testing was 0.086 mg with Site 20 sediments.
- 75. An obvious trend in the long-term leaching As data is the negative mass release. Twenty-seven sediment samples reduced the As concentrations in their respective site waters during 8 months of

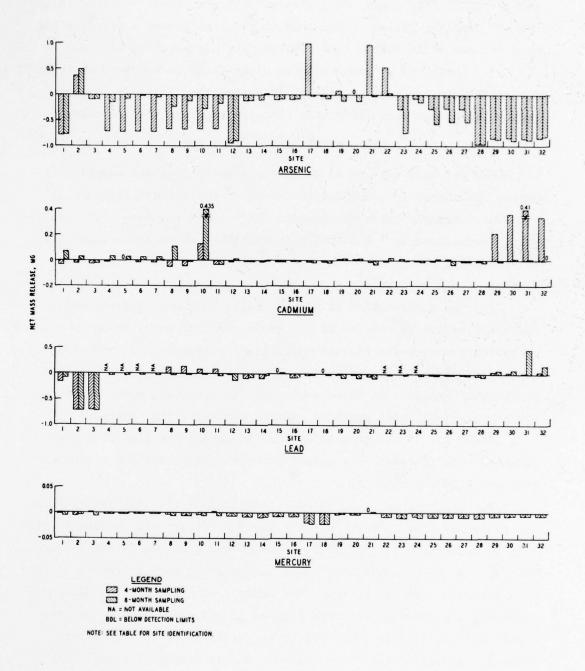


Figure 4. Net mass release of As, Cd, Pb, and Hg under quiescent aerobic conditions

leaching (Figure 4). Even among the five samples that demonstrated an As release during the study, four samples lost As between the 4-month and 8-month sampling periods. The lone sample that showed a positive net mass release of As during both sampling periods was from Site 2.

76. Long-term net mass release of As (RAS) in the 4-month leachate was related to net mass release of As during the Elutriate Test procedure (REAS) and water pH at the time of sampling (WPH) as shown below:

RAS (4 mos) = 2.414 + 6.161 REAS - 0.312 WPH  $R^2 = 0.5621$ 

Long-term net mass release of As in the 8-month leachate was significantly correlated (p < 0.05) with the pH of the 8-month leachate ( $r^2 = 0.336$ ). Arsenic concentrations in the 4-month leachate were significantly correlated (p < 0.05) with interstitial water As concentrations ( $r^2 = 0.503$ ).

### Cadmium

- 77. The distribution of Cd was unlike that of the previously discussed metals in that no Cd was extracted during the ammonium acetate or hydroxylamine hydrochloride extraction procedures. In addition, Cd concentrations were generally low in the interstitial water and DTPA extractable phases. In three instances, interstitial water concentrations exceeded 10  $\mu$ g/ $\ell$  and DTPA extract concentrations exceeded 0.1  $\mu$ g/g (Table 8). A net mass release of Cd during the Elutriate Test occurred with 12 sediment samples, but the release was low and never exceeded 0.004 mg (Site 19).
- 78. Observed net mass release of Cd during the leaching studies was generally minor except for five samples (Figure 4). Sediments from Site 10 released 0.1 mg Cd after 4 months and 0.435 mg Cd after 8 months. This was the only sample that had a positive net mass release value for Cd after each sampling period. Sediments from Sites 29, 30, 31, and 32 displayed a pronounced net mass release of 0.2 0.41 mg Cd in the 4-month leachate (Figure 4). The concentration of Cd in the 8-month leachate associated with each sediment sample dropped to less than initial site water concentrations (Tables Al, A2, and A3), resulting in a net mass release of essentially zero for the study period.

- 79. Cadmium concentrations in the 4-month leachate were significantly correlated (p < 0.05,  $r^2$  = 0.203) with Cd concentrations in the standard elutriate (Table A4). However, long-term net mass release of Cd was not related to any of the other parameters measured. Lead
- 80. Total concentrations of lead (Pb) in the sample sediments varied from 0.3  $\mu$ g/g (Site 1) to 523.4  $\mu$ g/g (Site 10). The highest concentrations of extractable Pb generally occurred in the DTPA extract with lesser amounts in the hydroxylamine extract and no Pb in the ammonium acetate extracts (Table 9). Net mass release of Pb during the Elutriate Test procedure ranged from -0.07 mg to 0.06 mg.
- 81. Only four sediment suspensions had a positive net mass release of Pb at the conclusion of the 8-month leaching study (Sites 29, 30, 31 and 32). The maximum positive net mass release of Pb was 0.49 mg Pb with Site 31 sediments (Figure 4). This was equivalent to a sediment release of 0.0022 mg/sq cm of Pb for the 8-month period. The largest negative net mass release of -0.75 mg Pb, -0.0034 mg/sq cm Pb, occurred with sediments from Sites 2 and 3 (Figure 4).
- 82. An analysis of the long-term and short-term leaching data suggests two mathematical relationships for Pb. The long-term net mass release of Pb in the 4-month leachate was significantly correlated (p < 0.01) with net mass release of Pb during the Elutriate Test procedure ( $r^2 = 0.581$ ). Long-term net mass release of Pb (RPB) was also related to both net mass release of Pb during the Elutriate Test procedure (REPB) and water pH (WPH) in the 8-month leachate as shown in the following regression equation:

RPB (8 mos) = -1.542 + 4.98 REPB + 0.185 WPH (8 mos)  $R^2 = 0.6695$  Mercury

83. Mercury (Hg) was the least abundant of the metals examined in this study. Total Hg concentrations ranged from <0.10  $\mu$ g/g (Sites 7, 23 and 28-32) to 2.01  $\mu$ g/g (Site 4) with only two sediments having more than 1.00  $\mu$ g/g Hg (Table 10). The low Hg levels were not extracted by ammonium acetate or DTPA, and the Hg concentrations in the

hydroxylamine hydrochloride extract only exceeded 0.1  $\mu g/g$  in three samples (Sites 4, 12, and 25). Net Mass release of Hg during the Elutriate Test procedure varied from -0.008 mg (Sites 23 and 24) to 0.0067 mg (Site 27).

84. Results of the long-term leaching of Hg from 32 sediment samples are presented in Figure 4. The obvious trend in the data is a negative net mass release as demonstrated by the fact that 60 of 64 samples had a negative net mass release. Long-term net mass release of Hg (RHG) was mathematically related to net mass release of Hg in the Elutriate Test procedure (REHG) and interstitial water Hg concentrations (IHG) as can be seen in the following regression equations:

RHG (4 mos) = 
$$0.002 - 6.88$$
 IHG +  $7.84$  REHG  $R^2 = 0.8567$  RHG (8 mos) =  $0.003 - 7.13$  IHG +  $7.80$  REHG  $R^2 = 0.8608$ 

There was very little change in net mass release of Hg between the 4-month and 8-month sampling periods. This is apparent from the similarity of the constants in the regression equations presented above and an inspection of Figure 4.

### Ammonium-N

85. Interstitial water and standard elutriates prepared with each of the 32 sediment samples were analyzed for ammonium-nitrogen (NH<sub>4</sub>-N), and the results are presented in Tables 12 and 13, respectively. Interstitial water NH<sub>4</sub>-N concentrations ranged from 2.1 mg/ $\ell$  (Sites 18 and 21) to 60.5 mg/ $\ell$  (Site 12) and 14 of the samples exceeded 10 mg/ $\ell$  NH<sub>4</sub>-N. Release of NH<sub>4</sub>-N during the Elutriate Test varied from 0.0 mg (Sites 28, 29, 30, 31, and 32) to 31.2 mg (Site 26). Calculated long-term net mass release of NH<sub>4</sub>-N during the 8-month leaching study is shown in Figure 5. A significant correlation (p < 0.01) was determined to exist between the long-term release and the interstitial water concentrations of the initial sediments. The coefficients for these relationships were r<sup>2</sup> = 0.5423 for the for the 4-month leaching results and r<sup>2</sup> = 0.492 for the 8-month leaching results.

# Nitrate + Nitrate-N

86. A high long-term net mass release of nitrate + nitrite

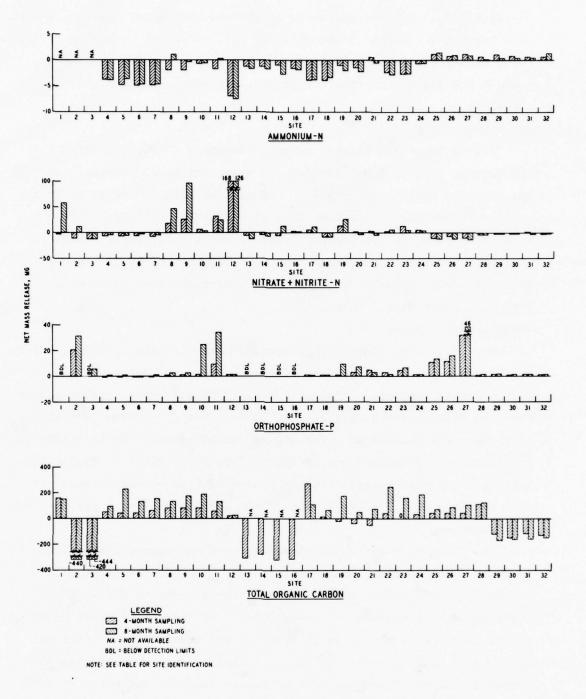


Figure 5. Net mass release of ammonium-N, nitrate+nitrite-N, orthophosphate-P, and total organic carbon under quiescent aerobic conditions

nitrogen ( $NO_3^- + NO_2^- - N$ ) was noted in the sediment/water leaching systems that reached a maximum of 168 mg (Site 12). However, no mathematical relationship was found between the long-term net mass release of  $NO_3^- + NO_2^- - N$  and any of the chemical or physical parameters measured in the study.

### Orthophosphate-P

87. A long-term release of orthophosphate  $(0-PO_4)$  occurred that was greater than or equal to zero for essentially all sediment samples and sampling periods (Figure 5). The maximum release was 46 mg in the sediment/water leaching system from Site 27. The calculated net mass release of  $0-PO_4$  in the 4-month leachate was significantly correlated (p < 0.01) with net mass release of  $0-PO_4$  during the Elutriate Test procedure  $(r^2 = 0.434)$ . The latter values ranged from -0.06 mg at Site 7 to 0.22 mg at Site 2 (Table 13).

### Total organic carbon

- 88. Total organic carbon concentrations were determined in interstitial water samples, standard elutriate preparations, and the long-term leaching samples. Interstitial water total organic carbon concentrations ranged from 6 mg/ $\ell$  at Site 19 to 206 mg/ $\ell$  at Site 14 (Table 12). Net mass release of total organic carbon during the Elutriate Test procedure varied between -44 mg (Site 2) to 14 mg (Site 9) (Table 13). Long-term net mass release (Figure 5) varied from -44 mg (Site 3) to +270 mg (Site 17) with two-thirds of the samples showing a positive net mass release.
- 89. Long-term net mass release of total organic carbon (Figure 5) in the 4-month leachate was significantly (p < 0.01) correlated (r<sup>2</sup> = 0.861) with net mass release of total organic carbon during the Elutriate Test procedure. Long-term net mass release of total organic carbon (RTOC) after 8 months of leaching was related to interstitial water total organic carbon (ITOC), net mass release of total organic carbon during the Elutriate Test procedure (RETOC), and water pH (WPH) as shown in the following regression equation:

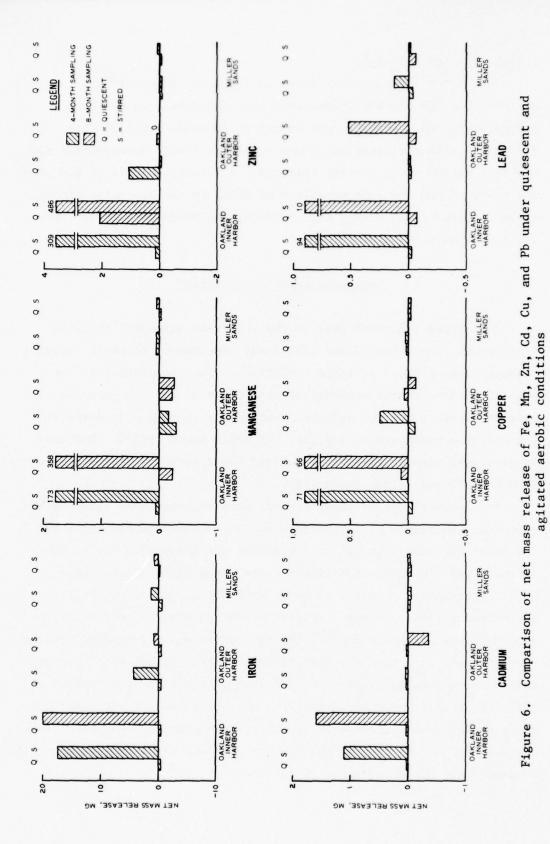
RTOC (8 mos) = 681.9 - 3.98 ITOC + 9.15 RETOC - 74.49 WPH (8 mos)  $R^2 = 0.8303$ 

## Polychlorinated biphenyls

90. After the long-term leaching study had been initiated, it was decided that PCB concentrations should be determined on selected leachate samples. However, the amount of leachate available for analysis was insufficient to ensure detection limits commensurate with the most recent water quality criteria. A detection limit of 2.0  $\mu g/\ell$  was achieved and the concentrations of PCB's in the leachates of sediments from the James River, Hudson River, and Duwamish Waterway were all less than this value.

# Long-Term Agitated Leaching

- 91. Three sediments used in the long-term quiescent leaching experiments were selected for additional observation of their leaching characteristics under agitated conditions. The preparation of the initial sediment/water suspensions were the same for the quiescent and agitated samples but the agitated samples were continually mixed with the aid of a motor-driven impeller for the 8-month period. Sediment samples used were obtained from Oakland Inner Harbor (19), Oakland Outer Harbor (20), and Miller Sands (28).
- 92. Comparisons of long-term net mass release under agitated and quiescent conditions of 12 parameters are presented in Figures 6 and 7. The least difference in net mass transfer was noted with Miller Sands sediment and the greatest difference was noted with Oakland Inner Harbor sediments. However, as shown in Table 14, pH of the stirred sediment-water mixture was 3.6 after 4 months compared to 8.0 for the same material incubated under quiescent conditions. Excluding Oakland Inner Harbor, long-term net mass release of Fe, Pb, and total organic carbon was generally greater under agitated conditions than under quiescent conditions. No attempt was made to correlate the net release under agitated conditions with the short-term chemical characterization of the sediments because of the limited data and the anomolous pH of the Oakland Inner Harbor sediment suspensions.



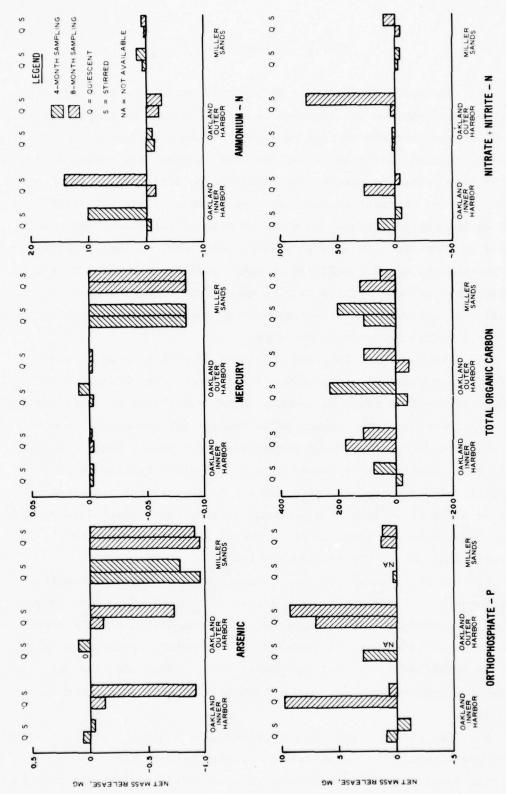


Figure 7. Comparison of net mass release of As, Hg,  $NH_4$ -N, orthophosphate-P, total organic carbon, and nitrate+nitrite-N under quiescent and agitated aerobic conditions

### PART V: DISCUSSION

- 93. Ecological evaluations of proposed discharges of dredged material are required for disposal in either inland<sup>2</sup> or ocean<sup>3</sup> waters. The Elutriate Test may be used in either of these evaluations. Total sediment chemical analysis may be used for disposal evaluation in inland waters when reviewing alternative sites for potential selection.<sup>2</sup>

  Total sediment chemical analysis is used because of its historical use with environmental samples, even though several literature reviews failed to demonstrate a relationship between total sediment analysis and the effects of that sediment on water quality. The Elutriate Test, although new and essentially untried when first used, was based on mobility of contaminants in sediment-water mixtures, approximating their ratios in hydraulic dredging operations.
- 94. The Elutriate Test was developed in part because it was reasoned that chemical contaminants would have to be released from dredged material in order to produce an adverse effect on water quality. However, there was some concern as to whether the release of chemical contaminants during the 30-min period specified in the Elutriate Test would be indicative or representative of long-term release after disposal. The purpose of this study was to observe the long-term release of 12 parameters from sediment samples under controlled conditions and compare the release with several short-term chemical characterizations of the same sediments.
- 95. An analysis of the data indicated that several mathematical relationships existed between the long-term release of several parameters, expressed on a mass and/or concentration basis, and the short-term extracts of the initial sediments. Parameters for which a mathematical relationship existed are summarized in Table 15. The specific regression equations and/or correlation coefficients were given in PART IV.
- 96. Two generalizations are indicated in Table 15. The first is that more mathematical relationships existed between the 4-month leaching results and the short-term chemical characterizations than with

the 8-month leaching results. Eighteen relationships existed at the end of 4 months which decreased to 8 after 8 months, suggesting that the importance of release due to initial mixing decreases and the importance of other factors is increased with the passage of time. A second generalization is that the Elutriate Test and the interstitial water analyses were more useful in predicting the long-term release than the other short-term tests. Forty-two percent (11 out of 26) of the calculated regression equations and/or correlation coefficients involved Elutriate Test results and an additional 27 percent (7 out of 26) involved interstitial water analyses. The hydroxylamine hydrochloride extract, ammonium acetate extract, DTPA extract, and the total digest accounted for a combined total of 31 percent (8 out of 26) of the statistically significant relationships that were found.

97. Results of this study have shown that net mass release of chemical constituents during short-term sediment leaching were related to long-term net mass release of chemical constituents under chemical conditions similar to those found near the sediment water interface at aquatic disposal field sites. It should be emphasized, however, that these relationships, developed under laboratory conditions, have not been field verified, and considering the difficulty of field studies of this nature, may never be verified. Nevertheless, the relationships found during this study will be of value in determining the potential for net mass release of chemical constituents from sediments following aquatic disposal.

# Factors Affecting Long-Term Net Mass Release

### Initial mixing and diffusion

98. Total sediment chemical constituent concentrations were not related to long-term net mass release of any of the chemical constituents determined in the leachate with the exception of Fe in the 8-month leachate and Mn in the 4-month leachate. However, long-term net mass release of chemical constituents was more frequently related to extracts that measure the more mobile sediment constituent phases. As discussed

earlier, these are the standard elutriate and interstitial water extracts.

- 99. The initial mixing of the sediment and water in the leaching columns was similar to the Elutriate Test procedure and ensured that the rate of release of chemical constituents was controlled by the exchange reaction rather than the hydrodynamics of the system. The relationship between net mass release of As, Cu, Pb, Hg, total organic carbon, and orthophosphate in the 4-month leachate and during the Elutriate Test procedure indicated that the exchange reaction during initial mixing was one of the dominant factors affecting release of these constituents for at least 4 months following initial mixing. For some constituents, such as Cu, Pb, Hg, and total organic carbon, the exchange reaction during initial mixing was still a significant factor related to net mass release in the 8-month leachate.
- 100. The results incleated that the effect of the exchange reaction during initial mixing on long-term net mass release was shifting to other factors as time of contact increased. Long-term net mass release of constituents such as orthophosphate, Pb, and total organic carbon was related exclusively to Elutriate Test procedure net mass release in the 4-month but not in the 8-month leachates. This shift may have been due to any number of factors that could regulate the concentrations of released constituents in the overlying water or change constituent release rates at the sediment water interface. The net effect was a reduction in the significance of the initial exchange reaction as a factor affecting net mass release with increasing time.
- 101. Following the initial mixing and settling of the sediment water mixtures in the leaching columns, exchange of chemical constituents occurred almost exclusively across an undisturbed sediment water interface. The factors that would become important under these conditions are specific ion mobility (diffusion) and concentration gradients. Also, in an oxygenated water system such as that in the leaching columns, a thin oxidized zone may exist on the sediment surface. Many workers have shown that an oxidized sediment surface layer can act as a barrier to the transfer of chemical constituents from sediments to the overlying water. 6,7,8

- 102. The existence of a surface-sediment oxidized layer does not, however, stop migration of chemical constituents from occurring within the sediments. It has long been known that Mn in sediments can migrate upward into the sediment-oxidized layer where precipitation to the more insoluble Mn +4 form may occur. 44,45,46 Others have shown that upward migration of  $\mathrm{Cu}^{47}$  and  $\mathrm{NH}_\Delta - \mathrm{N}^{48}, ^{49}$  will occur in lake sediments. Cline and Upchurch 47 have postulated that the upward migration of Cu occurred because of dewatering due to compaction and unidirectional ion migration; but migration of Cu and other heavy metals appeared to be due, to a much greater extent, to a bacterial mechanism. Copper migration ceased when the aerobic, biologically active portion of the sediment was reached. The Cu was immobilized by formation of a new complex or inorganic precipitate. The mobility of Cu and other metals that form insoluble sulfide compounds will be severely hindered in anaerobic sediments when large quantities of sulfate are present and are reduced to sulfide. 50,51
- 103. Results of this and other studies have shown that although the surface sediment-oxidized layer may decrease the flux of chemical constituents into the overlying water, the movement of materials into and out of the sediments does not cease. The kinetics of Mn +2 precipitation  $^{52}$  are such that some quantity of Mn $^{+2}$  can move through the sediment-oxidized layer and into the overlying water. Graham et al. $^{24}$ observed a flux of dissolved Mn into Narragansett Bay bottom waters of 2 + 1  $\mu g$  cm<sup>-2</sup> day<sup>-1</sup>. However, Mn mass balance in Narragansett Bay was conservative with no major net input or removal through interaction with Bay sediments. Precipitation of released Mn to insoluble MnO, at a rate comparable to its flux across the sediment-water interface was advanced as a possible reason for the observed conservative mass balance. 24 It is probable that the conservative behavior (relationship with Elutriate Test procedure net mass release) of Cu and other constituents in the long-term leachates was due to a mechanism similar to that advanced by Graham et al. 24
- 104. The strong relationship between interstitial water  $\mathrm{NH}_4$ -N concentrations and net mass release into the 4- and 8-month leachates

suggested that the sediment interstitial water was exerting a continuing influence upon the overlying water. The finding is supported by the work of Byrnes et al.,  $^{53}$  who showed that sediment  $\mathrm{NH_4-N}$  (interstitial and exchangeable) rapidly reaches equilibrium with the overlying water and that much of the  $\mathrm{NH}_{\Lambda}-\mathrm{N}$  mineralized in the sediment is soon returned to the overlying water. The relationship between interstitial water  $\mathrm{NH}_{\lambda}$ -N concentration and long-term net mass release of  $\mathrm{NH}_{\lambda}$ -N was almost certainly not an artifact of the initial sediment water exchange. Results of the Elutriate Test procedure indicated that massive releases of NH,-N occurred, in sharp contrast to the low releases observed over the long term. The most probable fate of the initially released  $NH_{\lambda}-N$ was nitrification followed by denitrification as the  $\mathrm{NO}_3$ -N diffused into contact with the reduced sediment, although the aeration procedure may have removed additional  $\mathrm{NH_4-N}$  by stripping. Engler and Patrick  $^{54}$  showed that NO<sub>3</sub>-N in floodwaters overlying swamps, marshes, and flooded soils is subject to rapid denitrification. Graetz et al. 55 found rapid denitrification in water overlying reduced sediments. With nitrification and denitrification a continuing sink for released NH,-N, the interstitial water served as a continuing source of NH,-N. Releases were of minor magnitude, however, for heavy losses of  $\mathrm{NH}_{\Delta}\mathrm{-N}$  are encountered due to nitrification and denitrification as the NH,-N diffuses through the oxidized-sediment layer and into the overlying water. 48,49

### Conductivity

105. Conductivity generally increased with time in the leachates (Table 11). The results, however, indicated that conductivity, a rough measure of leachate ionic strength, exerted little discernable effect on the long-term net mass release of most chemical constituents determined. Leachate conductivity was related only to net mass release of Fe in the 4-month leachates in addition to net mass release during the Elutriate Test procedure. While it is realized that conductivity (ionic strength) changes can alter the sorption-desorption tendencies of chemical constituents by varying the competition for sediment exchange sites, changes of the magnitude observed in this study were not a significant factor

affecting long-term net mass release of the chemical constituents analyzed.

## Leachate pH

106. The results indicated that leachate pH became a significant factor affecting net mass release as time of leaching increased. Net mass release of four parameters was correlated with the pH in the 8-month leachate, although no relationships were found during the earlier sampling period. Two parameters, Fe and Pb, were directly related to changes in pH while the other two parameters, As and total organic carbon, were inversely related to pH changes. The mechanisms by which leachate pH was affecting long-term net mass release were not readily apparent from the available data. It is known, however, that pH changes can alter the solubility of some salts as well as the species distribution of inorganic <sup>56,57</sup> and organic complexes in water.

## Agitation

107. It has been reported that agitation of sediment water mixtures will result in greater release of chemical constituents compared to incubation under quiescent conditions.  $^{5,59}$  Iron, lead, total organic carbon, and NO $_3$  + NO $_2$ -N results of this study have generally agreed with these findings. Inorganic N (NH $_4$ -N + NO $_3$ -N + NO $_2$ -N) net mass release after 8 months of incubation was greater under agitated than under quiescent conditions for Oakland Outer Harbor and Miller Sands sediments. This agreed with results reported by Lee of increased N release from Lake Mendota sediments under agitated compared to quiescent conditions. Net mass release of N in the quiescent columns may have been underestimated since evolution of gaseous N was not monitored and NO $_3$ -N can be rapidly reduced by denitrification.

108. Inorganic N net mass release at the end of 8 months was greater for Oakland Inner Harbor sediments incubated under quiescent rather than agitated conditions. This was apparently due to the pH (3.6) of the agitated sediment water mixture. It appeared that mineralization of organic N to NH<sub>4</sub>-N was inhibited in the Oakland Harbor slurry. At pH's below 6, NH<sub>4</sub>-N oxidation to NO<sub>2</sub>, a precursor to NO<sub>3</sub> is inhibited. Of If mineralization were proceeding normally, a buildup of

 $\rm NH_4-N$  should have occurred in the agitated sediment slurry. No such accumulation of  $\rm NH_4-N$  was noted in the agitated slurry.

- 109. These results, showing higher N release in sediment water mixtures at neutral to basic pH's compared to acidic conditions, agree with the findings of Austin and Lee. <sup>15</sup> They found that agitated,  $\text{CaCO}_3$ -buffered Trout Lake sediments, incubated at pH 7.7 for 25 days, released approximately twice as much N (NH<sub>4</sub>-N + NO<sub>3</sub>-N + NO<sub>2</sub>-N) as unbuffered Trout Lake sediments where the pH fell from 6.6 to approximately 4.7 after 25 days of incubation under aerobic, agitated conditions.
- 110. With the exception of As, Hg, O-PO $_4$ , NO $_3$  + NO $_2$ -N, and total organic carbon, most chemical constituents were released in larger quantities from Oakland Inner Harbor sediments under agitated conditions. This release was due to the low pH (3.6) of the agitated suspension which served to solubilize many metal compounds. Gambrell et al. have found that decreasing pH at a fixed Eh served to increase the water-soluble concentrations of many sediment-bound heavy metals.
- 111. The results indicated that few apparent differences were observed for net mass release of Mm, Zn, Cd, Cu, As, Hg, NH<sub>4</sub>-N, and O-PO<sub>4</sub> from Miller Sands and Oakland Outer Harbor sediments incubated under quiescent and agitated conditions. This indicated that the chemistry of the water rather than exchange reactions between water and sediment was the most important factor regulating long-term net mass release of Mn, Zn, Cd, Cu, As, Hg, NH<sub>4</sub>-N, and O-PO<sub>4</sub> from these sediments. From these results, admittedly based on only two samples, it appears that maximum net release of these constituents under laboratory conditions could be approximated under quiescent as well as agitated conditions.
- and quiescent conditions indicated that the most consistent change in leachate characteristics due to agitation was an increase in conductivity. Compared to the pH achieved under quiescent conditions (7.7-8.0), the low pH in the agitated Oakland Inner Harbor sediment slurry (3.6-3.7) was probably due to long-term oxidation of reduced sulfur compounds to sulfate. A second short-term water leach of Oakland Inner Harbor

sediments resulted in very little drop in solution pH.

- 113. The impact of benthic organisms upon long-term net mass release was not assessed in this study. There does exist some doubt, however, as to the comparability of sediment agitation by organisms and mechanical means. Rhoads  $^{63}$  has observed that burrowing polychaete worms found in soft, muddy substrate can greatly affect the chemistry of pore waters and sediments both by ingestion of sediment particles and by irrigation of the sediment with overlying water. Renfro  $^{64}$  has observed that polychaete worms can transfer large quantities of Zn from sediments into the overlying water, presumably by ingestion and solubilization.
- 114. With the exception of the Oakland Inner Harbor agitated slurry, where the drop in pH largely contributed to the differences in net mass release under agitated and quiescent conditions, agitation apparently had only a minor impact on long-term net mass release of most chemical constituents. The exposure of more sediment surface to leaching during agitated conditions was apparently of only short-term significance in increasing the net mass release of most constituents from sediments, specifically Oakland Outer Harbor and Miller Sands sediments. Time of contact
- 115. Time as a factor influencing long-term release from sediments is dependent upon the chemical parameter being discussed and several physical factors. For example, during the initial period of high mixing, the transfer of readily soluble constituents would be favored unless the leachate were already saturated with respect to that parameter. Time would not be expected to exert a large effect on the release of these parameters. However, for constituents that must undergo some type of hydrolysis reaction prior to release, time could exert a much larger effect. Also, once initial mixing is completed and the sediments settle to the bottom of the leaching container, mass transfer becomes a diffusion process and dependent upon time.
- 116. Leachate sampling at only 4- and 8-month intervals following leaching column setup rendered evaluation of detailed release patterns difficult. However, for constituents such as As, Pb, Hg, and NH<sub>4</sub>-N, which showed few differences in net mass release between the 4- and

8-month samples, it can be surmised that equilibrium or steady state conditions had been achieved prior to the 4-month sampling. An inspection of Figures 3-5 reveals that the remainder of the parameters monitored in this study demonstrated variable behavior.

117. Probably the most important effect of time seen in this study is that the composition of the initial sediments became less important with the passage of time. This is illustrated by the fact that 18 correlations were found between the 4-month release and the short-term sediment characterization. After 8 months, this number had been reduced to 8. A major reason for this shift is that the fate of a leached constituent is a function of the aquatic chemistry of that parameter rather than the source of the parameter. For example, NH<sub>4</sub>-N may be readily released from sediments but it is also denitrified in the overlying water, and Mn can reach elevated concentrations in the interstitial water of reduced sediments but it is also subject to oxidation and precipitation in oxygenated water. Thus, types of chemical reactions and reaction rates become more important than initial release in determining net mass release as the contact time between sediments and water increases.

# Magnitude and Significance of Long-Term Releases

orthophosphate-P showed the most consistent long-term net mass release from sediments to water. This implies that dredged sediments from the sites used during this study could generally act as a source of these constituents to the overlying water. The release of Zn disagreed with the findings of Duke et al., 65 who found that water-soluble radioactive Zn moved rapidly to the sediment and biota but that the exchange of sediment-sorbed radioactive Zn back into the water was relatively slow. The release observed in this study may have been due to the lack of biota in the water or the use of differing sediment-water systems. However, results of this study agreed with the findings of Chen et al. 9 that large quantities of Zn are released into the overlying water from

sediments incubated under aerobic quiescent conditions.

- 119. The maximum net release of Zn observed during the leaching period would not be expected to have a significant impact on water quality at the disposal site. The largest Zn release in the leaching column was 2.20 mg or 98.2 mg Zn/sq m over an 8-month period (0.41 mg Zn/sq m/day. Assuming that the disposal site water column was 10 m in depth and completely mixed, the released Zn would amount to an additional 9.8  $\mu g$  Zn/ $\ell$  during an 8-month period. This value would be conservatively high since dilution and other current effects over the 8-month period have been neglected. A direct assessment of the calculated Zn increase is not possible because the most recent Federal Zn criteria is one-tenth of the 96-hour LC  $_{50}$ . However, published LC  $_{50}$  values for Zn generally range from 0.5 mg/ $\ell$  to 5.0 mg/ $\ell$ , depending on the organism used in the test.
- 120. Release of orthophosphate-P (O-PO $_4$ ) into water from sediments under aerobic conditions such as was observed in this study has also been reported by other workers. Rowe et al.  $^{67}$  observed an average flux of O-PO $_4$  under aerobic conditions from sediments off Spanish Sahara of 0.005 µg m $^{-2}h^{-1}$ . Spear,  $^{68}$  Bortleson,  $^{69}$  and Sridharan have all observed appreciable O-PO $_4$  release from sediments under aerobic conditions. Pomeroy et al.  $^{50}$  have found that the exchange of O-PO $_4$  between sediments and waters consisted of a two-step ion exchange between clay minerals and water, plus an exchange between interstitial microorganisms and water.
- 121. The 0-PO $_4$  release rate during the long-term leaching study ranged from -0.3 µg 0-PO $_4$ /sq m/day to + 11.9 µg 0-PO $_4$ /sq m/day. The maximum observed concentration of 0-PO $_4$  was 4.29 mg/ $\ell$  and an additional 11 samples exceeded 1.0 mg 0-PO $_4$ / $\ell$  (Tables A2, A3). At this time there is no recommended 0-PO $_4$  water quality criteria, although a value of 0.025 mg/ $\ell$  0-PO $_4$  has been suggested for lakes and reservoirs because excessive concentrations may stimulate the growth of nuisance aquatic organisms. However, care similar to that taken with Elutriate Test results 1 must be exercised when interpreting the significance of high nutrient concentrations in the long-term leachates.

For example, Shuba et al.  $^{72}$  has shown that exposure of algal cells to standard elutriate for 7-21 days has produced stimulatory, inhibitory, and toxic responses. The problems with this approach is that Lee et al.  $^{73}$  and May  $^{74}$  have reported dredged material perturbations to only last 30 min to 2 hr in the field due to a high rate of dilution. Thus, when Plumb  $^{71}$  incorporated a dilution sequence into the algal bioassay procedure, it was shown that elutriates with high nutrient concentrations would not be expected to have a significant effect on the algal population. Hannah et al.  $^{75}$  has also reported no relationship between sediment compositions, elutriate composition, and effects on algal cultures.

- 122. Mercury and As showed the greatest affinity for sediments. No Hg release was observed and As release occurred from only five sediments. Sediment-bound As and Hg should therefore pose very few problems to long-term water quality.
- 123. The limitations of water quality standard comparisons and the care that must be used in applying water quality standards are well illustrated by the Hg and As results. Mercury leachate concentrations exceeded the EPA water quality criteria for protection of freshwater  $(0.05 \, \mu g/\ell)$  and marine  $(0.10 \, \mu g/\ell)$  aquatic life in almost all leachates where instrument detection limits (0.2  $\mu g/\ell$ ) permitted evaluation of the leachate Hg concentrations. However, the results also indicated that no net release of Hg from sediments to water occurred for sediments from any site. Disposal and long-term exposure of water to the dredged material actually lowered the overlying Hg concentrations in all cases, improving the quality of the overlying water with respect to Hg. A similar situation was found for leachate As. No firm criteria is available for As, although the EPA has stated that the existing data indicates that the 50  $\mu g/\ell$  As criterion established for domestic water supplies should be protective of aquatic life. 66 In only two of the six leachates that exceeded an As concentration of 50  $\mu g/\ell$  was net mass release from the sediments observed, indicating that water quality had been improved by exposure to the sediments in all but two cases.
- 124. Manganese and  $\mathrm{NH_4-N}$  showed very little long-term net mass release even though large quantities of these materials were released

during the Elutriate Test procedure and presumably during the initial mixing process. Manganese could have been lost from the water by precipitation of released Mn as insoluble MnO<sub>2</sub>. This occurs under the dissolved oxygen and pH conditions found in the leaching column waters. Ammonium—N may have been lost from solution by incorporation into bacterial cells, by nitrification followed by denitrification in the sediment, or by gas stripping as a consequence of the aeration process in the leaching containers.

- 125. A worst case evaluation of the potential chronic impact of Fe and NH<sub>4</sub>-N concentrations in the 4-month leachates demonstrated that these parameters did not exceed water quality criteria established by the U. S. EPA for protection of freshwater or marine organisms. Leachate Mn concentrations did not exceed marine water quality criteria, but one sample exceeded the Mn drinking water criteria of 50 mg/ $\ell$ . Twenty-two Cd 4-month leachate concentrations exceeded the most stringent Cd criteria of 0.0004 mg/ $\ell$ , but 20 initial water samples also exceeded this value.
- 126. The above comparison suggests that open-water disposal of dredged material would not be expected to have a significant adverse impact on water quality with respect to NH<sub>4</sub>-N, Fe, Mn, and Cd. The evaluation is considered conservative for several reasons: (a) chronic criteria based on lifetime exposure were used, (b) dredged material disposal distrubances in the water column only persist 30 min to 2 hr, and (c) the effects of mixing and dilution were not considered.
- 127. From the Zn, Cu, and Pb data available, it is impossible to evaluate leachate quality in relation to the EPA water quality criteria. Concentration levels in the EPA water quality criteria are one-tenth of the 96-hr  ${\rm LC}_{50}$  concentration, and such bioassay data are unavailable for the leachates generated in this study.
- 128. Comparisons of chemical constituent concentrations in the leachate with applicable water quality criteria have been intended to illustrate the significance of the chemical releases observed and to illustrate some of the pitfalls inherent in injudicious application of criteria. Even in these worst case situations, most constituents for which criteria were available rarely exceeded chronic water quality

criteria. In the case of Hg, which almost always exceeded water quality criteria, exposure of the water to the sediments had consistently lowered Hg concentrations in the water. When the probable mixing and dilution of released sediment constituents with disposal site water is considered, it is unlikely that any differential long-term adverse effects on water quality would occur because of aquatic disposal of these dredged sediments.

### PART VI: CONCLUSIONS AND RECOMMENDATIONS

## Conclusions

- 129. Net mass release of 12 chemical constituents from a variety of sediments under chemical conditions similar to those at open-water disposal sites was observed for a period of 8 months. This information, along with the results of 6 short-term characterizations of the same sediments, was subjected to correlation analyses and regression analyses. The results demonstrate that no single short-term test is capable of predicting the long-term water quality impacts of dredged material disposal. However, of the tests considered, the Elutriate Test appears to be most useful in assessing water quality problems since it was related to 7 parameters (Cu, As, Cd, Pb, Hg, P, total organic carbon) after 4 months of leaching and 4 parameters (Cr, Pb, Hg, total organic carbon) after 8 months of leaching. The next most useful test was interstitial water analysis the was related to 4 (Zn, As, Hg, NH,-N) and 3 (Hg, NH,-N, total organic carbon) parameters after 4 and 8 months of leaching, respectively. Total sediment analysis was only related to one constituent (Mn) in the 4-month leachate and one constituent (Fe) in the 8-month leachate.
- mixing of the sediment and water in the leaching columns was a significant factor affecting long-term net mass release. Thus, the greatest number of relationships were found between long-term net mass release and the short-term leaching procedures that extract the more mobile sediment constituents. These procedures were the interstitial water analysis, whose constituents would be rapidly released on mixing, and the Elutriate Test. As the length of time after initial mixing increased, the number of relationships between long-term release and short-term extracts decreased. This is attributed to an increase in the significance of the aquatic chemistry of each constituent.
- 131. Long-term net mass release of Mn,  $\mathrm{NH_4}-\mathrm{N}$ , Zn, Cd, Cu, As, Hg, and O-PO $_4$  from Oakland Outer Harbor and Miller Sands sediments were

similar under both agitated and quiescent incubation. This implies that the long-term net mass release of these constituents was controlled by the aqueous chemistry of each rather than the exchange process. Throughout the entire study Mn and NH $_4$ -N demonstrated very little long-term net mass release, even though Elutriate Test results indicated that large quantities of these constituents were available. This is probably due to the loss of released Mn by oxidation and precipitation and the loss of released NH $_4$ -N by nitrification, denitrification, and/or gas stripping.

- 132. Leachate pH became a more significant factor in effecting long-term net mass release as time of contact between sediment and water in the leaching columns increased. Iron, Pb, As, and total organic carbon net mass release in the 8-month leachates were related to leachate pH.
- 133. Zinc, total organic carbon, and 0-PO<sub>4</sub> showed the most consistent long-term net mass release from sediments into the water column. Iron, total organic carbon, and NO<sub>3</sub> + NO<sub>2</sub>-N generally exhibited greater net mass release from sediments incubated under agitated conditions when compared with sediments incubated under quiescent conditions. On the other hand, very little net mass release of Hg, Pb, Cd, or As into the water column was observed, regardless of the composition of the sediments.
- 134. A worst case evaluation of the potential effects of dredged material disposal was conducted by comparing the results of the long-term leaching study with the most stringent water quality criteria available. Although this approach is very conservative because the criteria are based on lifetime exposures and dredged material disposal disturbances in the water column seldom last longer than a few minutes to a few hours, the results suggest that the sediments used in this study would not be expected to cause significant long-term water quality problems. This conservative approach is further emphasized by the fact that expected mixing and dilution at the disposal sites were not considered.

## Recommendations

- 135. When concern exists over possible long-term net mass release of chemical constituents into the overlying water at aquatic disposal sites, consideration of net mass release during the Elutriate Test procedure and other short-term extractants can provide useful information on the probable direction (i.e., sediment to water, water to sediment) of long-term net mass release. Of the procedures recommended for the ecological evaluation of proposed dredged material disposal operations, the relationships developed during this study demonstrate that the Elutriate Test is better than the total sediment analysis procedure for assessing long-term impacts on the water column. However, because the relationships are based on laboratory observations and have not been field verified, caution in their use is recommended.
- 136. More extensive studies comparing net mass release under agitated and quiescent conditions should be conducted. Additional study should prove or disprove the preliminary findings that long-term net mass release of many chemical constituents from sediments incubated under agitated and quiescent conditions do not apparently differ unless a large decrease in pH occurs in the agitated sediment-water system.
- 137. The effects of macrobenthic organisms on net mass release of chemical constituents from sediments should be quantified. The difference between net mass release during mechanical agitation and biological agitation (organisms reworking the sediments) should be investigated.

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Table 1

Key to Site Numbers

	Site Location
1	Pensacola, Florida
2	Mobile Bay, Alabama
3	Mobile Bay, Alabama
4	Duwamish Waterway, Washington
5	Duwamish Waterway, Washington
6	Duwamish Waterway, Washington
7	Duwamish Waterway, Washington
8	Branford Harbor, Connecticut
9	Branford Harbor, Connecticut
10	Bridgeport Harbor, Connecticut
11	Bridgeport Harbor, Connecticut
12	Milwaukee Harbor, Wisconsin
13	Ashtabula Harbor, Ohio
14	Ashtabula Harbor, Ohio
15	Ashtabula Harbor, Ohio
16	Ashtabula Harbor, Ohio
17	James River, Virginia
18	James River, Virginia
19	Oakland Inner Harbor, California
20	Oakland Outer Harbor, California
21	Hudson River, New York
22	Terry Creek, Georgia
23	Brunswick Harbor, Georgia
24	Buttermilk Sound, Georgia
25	Houston Ship Channel, Texas
26	Houston Ship Channel, Texas
27	Houston Ship Channel, Texas
28	Miller Sands, Oregon
29	Columbia River, Oregon
30	Columbia River, Oregon
31	Columbia River, Oregon
32	Columbia River, Oregon

Table 2

Physical and Chemical Characteristics of the Dredged Material

Cation Exchange Capacity Meq/100g	0.4	26.8	26.2	22.5	38.9	27.1	5.1	9.9	35.0	45.5	38.9	25.9	14.1	16.8	12.2	7.7	26.9
Percent Clay	12	25	28	40	43	43	17	61	63	52	57	77	73	70	75	75	53
Percent Silt 2-50 um	1	20	40	20	25	20	1	1	25	43	43	18	20	23	18	18	30
Percent Sand	87	55	2	40	32	37	82	38	12	5	0	38	7	7	7	7	17
Total Inorganic Carbon Percent	0.18	0.19	0.45	0.25	0.13	0.09	0.62	0.36	0.18	0.86	0.19	4.62	0.12		97.0	1.00	0.00
Total Organic Carbon Percent	0.09	0.82	2.74	1.42	2.84	1.98	0.84	4.26	5.12	6.03	6.16	7.29	0.92		2.44	2.58	3.13
Total Phosphorus	13	259	729	710	858	887	561	2760	2005	1230	931	3131	364		777	979	1096
Total Kjeldahl Nitrogen	186	283	1877	828	1090	1090	375	3061	3288	3867	503	2447	076		1822	1189	2201
Sample Number	-	2	3	4	2	9	7	8	6	10	11	12	13	14	15	16	17

(Continued)

Table 2 (Concluded)

Cation Exchange Capacity Meq/100g	61.9	6.44	32.5	99.5	5.4	108.5	0.3	36.3	59.2	59.3	6.4	5.2	4.8	5.2	4.7
Percent Clay <2 µm	32	87	43	20	18	17	12	47	37	37	12	12	12	14	14
Percent Silt 2-50 µm	89	45	07	80	10	83	1	43	53	53	1	1	1	1	1
Percent Sand >50 µm	0	7	7	0	72	0	87	10	10	10	87	87	87	85	85
Total Inorganic Carbon Percent	0.01	0.27	0.08	90.0	0.22	0.00	0.02	0.50	0.74	0.65	0.03	0.05	0.03	0.00	0.00
Total Organic Carbon Percent	2.01	3.94	1.69	4.67	4.87	3.95	0.14	1.68	3.24	4.22	0.13	0.10	90.0	0.04	0.16
Total Phosphorus ug/g	918	649	588	510	1092	884	40	558	3898	2603	268	447	457	442	425
Total Kjeldahl Nitrogen µg/g	1714	2149	1555	874	3496	3598	124	1523	2200	2531	114	98	98	98	115
Sample Number	18	19	20	21	22	23	24	25	56	27	28	53	30	31	32

Table 3

Sediment Copper Concentrations and Net Mass Release of Copper During the Elutriate Test Procedure

Sampling Site	Elutriate Net Mass Release mg	Interstitial Water mg/1	Ammonium Acetate Extractable µg/g	Hydroxylamine Extractable µg/g	DTPA Extractable µg/g	Total Digest µg/g
1	0.005	NE	ŅE	NE	0.02	0.33
2	0.004	0.004			6.50	7.1
3	0.002	0.001			1.65	15.94
4	-0.003	0.023			65.30	194.3
5	0.001	0.002			62.00	262.9
6	-0.002	0.003		0.03	51.50	149.2
7	-0.003	NE	0.63	0.06	-	23.7
8	-0.002	0.002	NE	NE	95.10	369.8
9	0.001	0.003		NE	83.10	281.2
10	-0.004	0.003		NE	8.10	1446.0
11	0.004	0.003	1	0.16	1.40	667.5
12	NE	0.040	0.14	NE	21.20	59.5
13	0.001	0.003	NE	0.10	4.50	22.7
14	0.003	0.002		0.05	-	-
15	0.002	0.003		0.09	7.90	31.6
16	0.024	0.005		0.05	13.00	35.1
17	0.001	0.012	0.14	NE	11.50	26.1
18	0.011	0.001	0.00	NE	6.60	31.4
19	-0.003	0.013	0.93	0.38	92.60	217.3
20	0.004	0.007	NE	0.25	18.00	33.1
21	0.010	0.003		NE	4.30	26.4
22	-0.005	0.001		0.27	5.44	18.4
23	0.033	0.001	V	0.23	2.34	14.0
24	-0.001	NE	0.09	0.37	0.19	6.0
25	-0.050	0.005	NE	NE	5.95	17.0
26	-0.050	0.002	0.25		0.09	65.3
27	-0.050	0.005	NE		0.03	71.1
28	0.002	NE	0.06	V S	0.23	8.8
29	-0.001	NE	0.10	0.26	0.13	3.7
30	-0.002	NE	0.09	3.27	0.12	3.9
31	0.000	NE	0.40	0.09	0.12	3.5
32	-0.001	NE	1.49	0.38	0.12	3.4

Table 4

Sediment Iron Concentrations and Net Mass Release of Iron

During the Elutriate Test Procedure

Sampling Site	Elutriate Test Net Mass Release mg	Interstitial Water mg/l	Ammonium Acetate Extractable Pg/g	Hydroxylamine Extractable µg/g	DTPA Extractable µg/g	Total Digest ug/g
1	0.013	NE	4	1	4	14
2	4.14	4.46	3116	3199	3575	12,995
3	0.35	26.80	905	1847	729	19,140
4		1.40	1116	1730	513	17,897
5	0.12	2.52	572	4318	2049	23,118
6	0.10	1.79	1608	1861	1642	22,680
7	-0.01	NE	87	198	2912	9,789
8	1.05	8.19	1714	1881	3851	47,656
9	0.06	0.78	493	2482	5387	35,416
10		25.00	3349	6501	165	30,989
11	0.04	11.30	7312	7122	6306	12,690
12		123.00	1935	224	1181	12,601
13	0.25	81.00	3291	3699	499	30,303
14	0.81	74.00	4997	1492		
15	0.29	47.00	2090	1242	1006	30,555
16	0.04	19.00	1476	327	755	29,040
17	0.26	23.50	2251	4125	1764	30,710
18	0.62	7.50	4477	473	2081	38,010
19	0.00	4.30	1401	1838	2941	28,272
20	0.02	2.40	1240	1058	944	32,031
21	0.42	1.00	207	432	203	8,567
22		0.90	1148	2197	2712	25,432
23	0.07	52.50	2145	1742	3231	23,763
24	0.00	NE	1	47	21	470
25	0.02	0.79	783	479	1372	14,308
26	0.06	5.92	757	708	4767	18,279
27	0.04	0.65	445	564	4885	15,567
28	0.22	NE	7	122	53	7,914
29	0.02	NE	21	236	38	9,368
30	0.02	NE	25	288	32	9,547
31	0.02	NE	19	245	34	9,422
32	0.02	NE	17	344	32	8,819

Table 5
Sediment Manganese Concentrations and Net Mass Release of Manganese
During the Elutriate Test Procedure

Sampling Site	Elutriate Test Net Mass Release mg	Interstitial Water mg/l	Ammonium Acetate Extractable ug/g	Hydroxylamine Extractable ug/g	DTPA Extractable µg/g	Total Digest µg/g
1	0.06	NE	0.1	0.2	0.1	0.4
2	0.00	3.10	289.1	232.0	529.0	
3	0.50	30.00	128.9	168.0	40.0	416.7
4	0.37	2.60	18.1	12.0	24.0	199.0
5	0.78	0.60	22.5	28.0	12.0	226.0
6	3.59	0.85	25.5	23.0	15.0	250.5
7	0.02	NE	28.7	33.0	11.0	127.3
8	2.84	2.28	47.1	15.0	69.0	502.6
9	2.07	1.30	27.0	46.0	54.0	510.4
10	0.52	2.96	47.2	90.0	5.0	333.3
11	1.08	2.42		141.0	29.0	
12		0.60	84.5	48.0	16.0	494.9
13	1.84	10.50	177.4	185.0	78.0	262.6
14	3.87	15.30	449.2	213.0		
15	1.29	7.94	158.5	138.0	89.0	464.6
16	0.73	4.56	245.9	83.0	60.0	313.1
17	1.08	10.70	455.0	466.0	366.0	890.8
18	0.98	4.70	280.3	328.0	367.0	961.7
19	1.02	0.90	71.1	73.0	42.0	301.0
20	1.17	2.50	69.1	29.0	32.0	476.6
21	0.11	0.90	10.5	13.0	11.0	51.3
22	4.79	6.70	242.6	509.0	416.0	645.9
23	5.51	22.30	254.1		216.0	481.2
24	0.00	NE	2.7	8.0	1.2	20.0
25	23.54	27.50	675.6	438.0	578.0	962.7
26	1.22	2.50	102.7	88.0	96.0	279.6
27	1.39	0.85	58.7	55.0	43.0	137.4
28	0.01	NE	5.4	45.0	2.3	74.6
29	0.02	NE	12.3	22.0	1.0	57.1
30	0.03	NE	15.8	26.0	1.0	56.8
31	0.00	NE	11.5	25.0	1.1	115.3
32	0.01	NE	10.7	33.0	1.0	84.9

Table 6

Sediment Zinc Concentrations and Net Mass Release of Zinc

During the Elutriate Test Procedure

Sampling Site_	Elutriate Test Net Mass Release mg	Interstitial Water mg/2	Ammonium Acetate Extractable <u>Pg/g</u>	Hydroxylamine Extractable µg/g	DTPA Extractable µg/g	Total Digest
1	0.003	NE	0.2	0.9	0.5	1.6
2	1.050	0.040	9.8	17.1	27.6	80.5
3	0.045	0.080	0.9	NE	5.8	219.8
4	0.020	0.020	4.7	5.1	33.8	236.4
5		0.150	8.7	12.8	78.8	407.2
6	0.002	0.020	5.2	11.1	29.2	228.3
7	0.003	NE	7.7	9.3		39.1
8		0.170	1.9	12.2	141.1	768.2
9		0.560	1.4	NE	88.8	487.0
10	0.002	0.090	17.6	30.7	42.7	929.7
11		0.040	31.6	36.1	104.6	1505.0
12		0.220	5.2	3.2	66.7	338.4
13	0.005	0.020	9.5	22.3	3.2	85.8
14	0.042	0.210	19.4	4.0		
15	-0.012	0.130	5.7	3.5	5.9	131.3
16	0.057	0.350	9.3	2.8	12.8	134.8
17	-0.020	0.140	24.8	32.0	20.0	215.7
18	-0.033	0.660	8.0	13.5	6.5	142.8
19	-0.018	0.070	5.0	5.8	84.2	426.7
20		0.120	6.0	5.0	24.1	164.1
21	-0.009	0.210	3.3	6.8	95.8	97.4
22	0.0	0.020	3.5	9.8	8.4	61.1
23	-0.032	0.010	4.5	6.6	6.5	62.6
24	-0.043	NE	0.7	1.6		2.4
25	0.002	0.001	3.0	3.5	4.1	48.6
26	0.035	0.043	1.9	3.7	38.0	438.2
27	0.003	0.011	1.7	3.2	14.4	402.1
28	-0.02	NE	5.5	15.7	3.5	18.6
29	0.005	NE	1.6	6.4	7.3	5.1
30	-0.002	NE	2.8	11.7	3.1	9.8
31	0.007	NE	1.9	5.6	1.1	7.5
32	0.005	NE	3.9	7.8	4.1	24.8

Table 7
Sediment Arsenic Concentrations and Net Mass Release of Arsenic
During the Elutriate Test Procedure

Sampling Site	Elutriate Test Net Mass Release mg	Interstitial Watermg/l	Ammonium Acetate Extractable Pg/g	Hydroxylamine Hydrochloride Extractable ug/g	DTPA Extractable ug/g	Total Digest
1	-0.050	NE	0.03	0.23	0.02	0.45
2	-0.008	0.005	NE	NE	0.15	1.24
3	-0.008	0.008	0.07	0.29	0.02	2.50
4	-0.010	0.016	0.00	0.71	0.71	7.00
5	-0.078	0.021	0.15	NE	1.29	7.50
6	-0.078	0.024	NE	NE	1.33	6.75
7	-0.020	NE	NE	0.50	0.92	3.26
8	-0.070	0.021	NE	0.24	0.17	9.14
9	-0.070	0.081	0.27	1.97	0.31	6.25
10	-0.070	0.017	0.00	NE	0.04	4.95
11	-0.070	NE	0.46	2.18	0.24	3.48
12		0.014	NE	NE	0.16	3.54
13	-0.008	0.026	0.07	0.67	0.04	6.77
14	0.028	0.033	NE	0.21		
15	-0.009	0.032	0.03	0.19	0.06	7.47
16	-0.008	0.016	NE	0.18	0.19	7.52
17	0.020	0.082	NE	0.26	0.07	2.99
18	-0.008	0.007	NE	NE	0.07	4.49
19	-0.017	0.121	0.26	0.29	0.44	6.44
20	-0.086	0.064	0.29	0.12	0.28	9.06
21	0.020	0.003	NE	0.07	0.04	1.08
22	-0.008	0.095	0.10	2.71	0.55	8.94
23	-0.063	0.120	0.17	1.65	0.59	7.15
24	0.016	NE	0.13	0.04	NE	0.23
25	-0.025	0.099	0.13	NE	0.36	3.72
26	-0.024	0.005	0.09	0.22	0.29	6.18
27	-0.004	0.076	NE	0.31	0.27	7.47
28	-0.065	NE	NE	0.02	0.01	<0.25
29	-0.040	NE	NE	0.02	NE	<0.25
30	-0.040	NE	0.07	0.02	NE	<0.25
31	-0.020	NE	0.04	0.03	0.03	<0.25
32	-0.030	NE	0.05	0.05	0.01	<0.25

Table 8

Sediment Cadmium Concentrations and Net Mass Release of Cadmium

During the Elutriate Test Procedure

Sampling Site	Elutriate Test Net Mass Release mg	Interstitial Water mg/l	Ammonium Acetate Extractable µg/g	Hydroxylamine Extractable µg/g	DTPA Extractable µg/g	Total Digest
1	0.001	NE	NE	NE	0.07	0.12
2	-0.002	0.002			0.02	0.12
3	-0.002	0.003			NE	0.33
4	0.001	0.013			0.03	0.54
5	0.001	0.003			0.05	3.68
6	-0.003	0.003			0.03	3.07
7	0.001	NE				0.10
8	-0.004	0.006			0.10	7.92
9	-0.004	0.006			0.10	6.67
10	-0.001	0.007			NE	19.40
11	-0.005	0.003			3.00	53.30
12		0.005			3.90	15.50
13	-0.001	0.003			0.02	3.71
14	0.001	0.004				
15	-0.001	0.003			0.06	5.30
16	-0.001	0.003			0.04	4.80
17	0.000	0.002			0.02	5.02
18	0.000	0.020			0.02	4.77
19	0.004	0.003			0.09	5.92
20	-0.003	0.003			0.03	5.29
21	-0.004	0.001			0.08	15.23
22	0.003	0.008			0.05	4.57
23	0.002	0.008			0.04	4.57
24	0.003	NE			NE	0.50
25	0.001	0.005			0.01	3.22
26	0.000	0.030			0.16	9.03
27	0.001	0.006			0.01	7.78
28	0.001	NE			0.01	0.10
29	0.000				NE	0.03
30						0.05
31						0.05
32	1					0.05

Table 9

Sediment Lead Concentrations and Net Mass Release of Lead

During the Elutriate Test Procedure

Sampling Site	Elutriate Test Net Mass Release mg	Interstitial Water mg/l	Ammonium Acetate Extractable  µg/g	Hydroxylamine Extractable µg/g	DTPA Extractable µg/g	Total Digest
1	-0.008	NE	NE	NE	0.05	0.3
2	-0.070	0.005			13.27	17.5
3	-0.070	0.008			8.02	15.4
4	0.013	0.042			99.50	168.9
5	-0.001	0.007			118.00	253.8
6	1	0.063			152.00	262.9
7		NE				103.0
8		0.007			101.60	115.0
9	1	0.007			64.40	94.0
10	0.016	0.007			21.40	523.4
11	-0.001	0.022			267.30	314.7
12		0.098		0.93	80.90	127.5
13	-0.007	0.006		2.85	13.50	27.0
14	0.020	0.054		4.38		
15	-0.009	0.028		2.89	18.30	31.8
16	-0.009	0.007		4.70	19.80	78.0
17	0.060	0.250		3.55	26.90	44.7
18	-0.001	0.022		2.64	23.00	39.3
19	0.003	0.017		4.25	224.40	500.0
20	-0.001	0.022		NE	35.90	57.2
21	0.057	0.002		0.59	55.00	110.3
22	0.013	0.010		18.00	22.70	20.3
23	0.017	0.021		11.50	21.20	21.5
24	0.033	NE		0.18	0.10	0.4
25	0.008	0.010		9.20	21.90	22.6
26	0.008	0.122		9.90	93.10	229.3
27	0.057	0.010		9.80	32.80	250.5
28	0.001	NE		1.40	0.14	3.5
29	0.004			0.90	0.46	7.1
30	0.002			1.10	0.25	4.8
31	0.004			1.20	0.20	5.3
32	0.003	<b>†</b>	1	0.60	0.24	4.5

Table 10
Sediment Mercury Concentrations and Net Mass Release of Mercury
During the Elutriate Test Procedure

Sampling Site	Elutriate Test Net Mass Release mg	Interstitial Watermg/l	Ammonium Acetate Extractable ug/g	Hydroxylamine Hydrochloride Extractable µg/g	DTPA Extractable µg/g	Total Digest
1	0.0012	NE	NE	NE	NE	0.11
2	0.0003	0.002		NE		0.30
3	0.001	0.003		NE		0.11
4	0.002	0.003		0.140		2.01
5	0.001	0.003		NE		1.40
6	0.001	0.004				1.00
7	0.004	<u></u>				<0.10
8	0.0001	0.004				0.30
9	0.0055	0.003				0.60
10	0.0028	0.004				0.36
11	0.0001	0.004		1		0.64
12		0.001		0.120		0.60
13	-0.003	0.011		0.060		0.15
14	-0.001	0.005		0.060		
15	-0.003	0.007		0.040		0.80
16	-0.003	0.008		0.030		0.30
17	0.000	0.002		0.050		0.30
18	0.0003	0.002		0.070		0.20
19	0.000	0.001		NE		
20	0.000	0.002		NE		
21	0.0002	0.003		0.010		1.00
22	-0.006	0.002		NE		0.20
23	-0.008	0.002		0.005		<0.10
24	-0.008	NE		0.001		0.30
25	-0.002	0.007		0.111		0.20
26	-0.003	0.007		0.070		0.50
27	0.0067	0.004		0.070		
28	0.0034	NE		0.040		<0.10
29	0.0015			0.070		
30	0.0028			0.100		
31	-0.001			0.090		
32	0.0013	1	1	0.090	•	1

Note: 35 - none extracted.

Table 11

Conductivity and pH of Leaching Column Waters

Sample ID	pH 4-Month Sampling	pH 8-Month Sampling	Initial Conductivity mmhos/cm at 25°C	Four-Month Conductivity mmhos/cm at 25°C	Eight-Month Conductivity mmhos/cm at 25°C
1	8.1	7.6	29.90	22.40	26.50
2	8.2	7.2	0.14	1.43	35.00
3	8.0	7.7	0.14	3.72	35.00
4	8.2	8.0	34.50	38.76	41.30
5	8.4	8.1	34.50	37.74	37.10
5 6 7	8.5	8.0	34.50	35.70	38.20
7	8.3	7.8	34.50	34.70	37.10
8	7.8	7.9	35.65	31.60	36.70
9	7.7	7.9	35.65	32.20	42.10
10	8.2	8.1	35.65	31.20	37.80
11	8.1	7.8	35.65	31.20	46.40
12	8.3	7.9	0.49	0.96	1.30
13	7.0	7.5	0.48	0.56	0.59
14	6.9	7.6	0.48	0.50	0.49
15	7.1	7.9	0.48	0.51	0.56
16	7.5	7.9	0.48	0.45	0.53
17	6.6	7.4	0.22	0.51	14.0
18	6.8	7.4	0.22	0.42	13.0
19	8.0	7.7	42.50	25.50	36.70
20	8.1	7.8	42.50	25.50	50.80
21	8.0	6.5	0.18	-	0.28
22	6.4	7.4	13.90	26.00	36.70
23	7.5	8.1	31.90	32.20	36.4
24	7.7	8.1	5.06	29.10	26.0
25	8.0	7.9	31.90	35.40	40.00
26	8.0	8.2	31.90	33.30	37.80
27	8.0	8.2	31.90	34.20	38.90
28	6.8	8.7	0.17	2.50	0.40
29	7.7	8.4	27.50	36.00	37.40
30	7.7	8.5	27.50	33.90	37.40
31	7.7	8.4	27.50	35.00	38.50
32	7.6	8.4	27.50	30.70	35.40

Table 12

Concentrations of Nutrients in Dredged Material

Interstitial Water\*

Sample No.	NH <sub>14</sub> -N	Ortho- phosphate-P	Total Phosphorus	Total Organic Carbon
1				
2	2.22	0.85	1.10	18
3	37.10	0.11	0.86	46
4	2.62	0.13	0.24	12
5	3.43	0.56	0.70	22
6	8.58	0.76	1.17	24
7				
8	25.80	0.94	<u></u>	52
9	22.00	2.13	8.69	26
10	16.20	2.18	2.58	26
11	16.10	3.56		20
12	60.50	<0.01	16.00	56
13	24.20		1.72	61
14	17.80		0.55	206
15	8.80		0.55	105
16	18.00		0.31	33
17	5.60		0.31	25
18	2.10	0.01	0.39	57
19	2.60	1.05	1.42	6
20	8.10	5.71	5.79	16
21	2.10	0.58		20
22	19.10	9.27	11.20	19
23	24.10	0.45	1.17	34
24		~-		
25	32.70	9.63	10.70	20
26	48.00	8.91	9.42	20
27	55.00	11.40	12.70	24
28		_	- <del>-</del> -	
29				
30				
31				
32				1

<sup>\*</sup> Concentrations are stated in milligrams per litre

Table 13

Nutrient Net Mass Release\* During the Elutriate Test Procedure

Site	NH <sub>14</sub> -N	Ortho- phosphate-P	Total Organic Carbon
1	0.34	0.042	2
2	0.92	0.22	-44
3	4.45	0.0	-38
4	0.72	0.03	4
5	0.13	0.0	5
6	0.46	-0.02	2
7	0.46	-0.06	-2
8	2.80	0.13	4
9	6.25	0.13	14
10	4.06	-0.014	7
11	3.73	-0.015	8
12	<u></u>	<del></del>	<u></u>
13	3.51	0.0	<b>-</b> 25
14	4.81		1
15	4.74		7
16	3.11		-29
17	2.55		0
18	0.47	0.01	3
19	1.30	0.03	3
20	1.30	0.03	5
21	3.40	0.02	5
22	5.80	-0.03	-1
23	5.40	0.0	<b>-</b> 2
24	0.23	0.02	4
25	15.60	0.19	0
26	31.20	0.19	10
27	13.20	0.19	0
28	0.0	0.0	
29			-17
30			-18
31			-16
32	1	<b>†</b>	-13

<sup>\*</sup> Releases are stated in milligrams

Table 14
Conductivity and pH of the Agitated and Quiescent Leachates

		p		tivity s/cm	
Site	Treatment	4 months	8 months	4 months	8 months
Oakland Inner Harbor	Unstirred	8.0	7.7	26.0	34.0
Oakland Inner Harbor	Stirred	3.7	3.6	49.0	51.0
Oakland Outer Harbor	Unstirred	8.1	7.8	26.0	47.0
Oakland Outer Harbor	Stirred	6.8	7.6	26.0	52.0
Miller Sands	Unstirred	6.8	8.7	6.8	0.4
Miller Sands	Stirred	7.6	8.3	42.0	18.0

Table 15

Significant Statistical Relationships Between Long-Term Release and Short-Term Sediment Characterization Results

		Corre	lations B	etween S	hort-Term	Extract	ions and	Long-Terr	Correlations Between Short-Term Extractions and Long-Term Leachates of Contaminants*	of Contamin	nants*	
Test Procedure	3	된	짼	u <sub>Z</sub>	As	टुव	Pb	H.B.	N- <sup>†</sup> HN	NO3+ NO2-N	d.	TOC
				17	4-Month Sampling Interval	nling In	terval					
Elutriate	×				×	×	×	×			×	×
Interstitial Water				×	×			×	×			
Hydroxylamine			×									
Ammonium Acetate		×		×								
DTPA	×	×	×									
TOTAL			×									
				8	8-Month Sampling Interval	pling In	terval					
Elutriate	×						×	×				×
Interstitial Water								×	×			×
Hydroxylamine												
Ammonium Acetate												
DTPA												
TOTAL		×										

<sup>\*</sup> Entry X indicates significant (p < 0.05) relationship

APPENDIX A: CHEMICAL CONSTITUENT CONCENTRATIONS

Table Al

Initial Concentrations of Chemical Constituents in Leaching Column Water\*

130C 7 7 7 7		4-12	00	890,98	57288
Ortho- phosphate-P <0.03 <0.03 <0.03	0.52	0.032	0.02 0.02 0.13 0.13	<ul><li>0.01</li><li>0.03</li><li>0.03</li><li>0.01</li><li>0.01</li></ul>	0.01
NO3+NO2-N 0.25 1.26 0.56	0,40	1.11	1.04 1.04 0.66 0.66	0.62 0.26 0.26 1.33	0.62
NH <sub>1</sub> -N  <0.08 <0.08 <0.08  0.50	0.29	0.24	0.41 0.33 0.33 0.08	0.41	
Hg 0.0008 0.0009 0.0009	0.0008	0.0078	0.0023 0.0023 0.0005 0.0005	<pre>&lt;0.0002 0.0062 0.0082 0.0008 0.0007</pre>	0.0077
Ph 0.018 0.073 0.002		0.017	0.002	0.003 0.002 0.002 0.004	0.002
0.003 0.0024 0.0024 0.0024	0.0048	0.0014	0.0019 0.0019 0.0038	0.0049 0.0025 0.0026 0.0017	0.0043
As 0.080 0.010 0.010 0.080	0.073	0.098	0.010 0.010 0.098 0.098	0.016 0.073 0.099 0.017 0.014	0.098
Zn 0.002 0.029 0.029 0.002		0.040	0.050 0.050 0.015 0.015	0.074 0.029 0.056 0.056	0.005
Mn 0.0032 0.0235 0.0235 0.0076	0.0270	0.004	0.003 0.003 0.034 0.034	0.012 0.013 0.056 0.002 0.011	0.011
Fe 0.017 0.029 0.029	0.053	0.148	0.148 0.053 0.053	0.105 0.066 0.019 0.020	0.010
0.0060 0.0035 0.0035 0.0035	0.0081	0.0039	0.0028 0.0028 0.0099	0.0014 0.0077 0.0032 0.0030	0.053 0.0024 0.0049
Site 22 24 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	10 9 8	13 15 17 17 17 17 17 17 17 17 17 17 17 17 17	17 18 19 20	21 22 23 24 25	26 28 32 32 32 32

\* Concentrations in milligrams per litre

100	20 15 80 80 80 80 80 80 80 80 80 80 80 80 80	12 2 2 2 8 1 1 2 2 8 1 2 2 3 1 3 1 3 1 3 1 3 1 3 1 3 1 3 1 3	100 100 100 100 100 100 100 100 100 100	848	10 10 12 12	12 12 16 9	10
Ortho- phosphate-P	<pre></pre>	0.07 0.07 0.09 0.19	0.18	0.02	0.43 0.33 0.17 0.07	1.08 3.20 0.03 0.09	0.07
NO3+NO2-N	<0.01 0.12 0.15 <0.005	2.20 3.08 1.00	3.60 18.80 0.60 0.74	1.34 1.52 0.22 2.04 0.70	0.25 0.63 1.60 0.76 0.20	0.60 0.32 0.33 0.15	0.30
NH4-N	<pre>&lt;0.01 &lt;0.01 &lt;0.01 0.13 &lt;0.01 </pre>	<pre>&lt;0.01 &lt;0.01 0.10 0.10 0.23</pre>	0.13 0.13 0.12 0.12	0.09 0.03 0.02 0.23	0.15 0.19 0.06 0.04	0.09 0.12 0.08 0.12 0.09	0.00
H	0.0005	0.0004	0.0009 0.0008 0.0003 0.0002	0.0006			-
Pb	<0.002 <0.002 <0.002	0.015	0.010 0.015 0.001 0.001	<pre></pre>	0.006	<pre>&lt;0.001 &lt;0.003 0.003 0.005 0.005</pre>	0.003
Cd	<0.0001 0.0004 <0.0001 0.0021 0.0033	0.0015 0.0014 0.0004 0.0003 0.0180	0.0020 0.0004 <0.0001 0.0003	0.0003 0.0010 0.0040 0.0040	0.0038 0.0018 0.0036 0.0016	0.0045 0.0038 0.0012 0.0250	0.0380
As	0.002 0.047 0.001 0.008	0.007	0.004	0.003 0.112 0.008 0.105	0.115 0.127 0.072 0.010	0.049 0.048 0.002 0.004 0.005	0.005
Zn	0.085 0.123 0.074 0.062 0.040	0.042 0.052 0.019 0.005	0.018 0.005 0.009 0.009	0.005 0.266 0.027 0.026	0.030 0.004 0.022 0.022	0.010 0.021 0.030 0.005	0.006
Ā	0.002 0.056 0.005 0.001	0.001 0.002 0.006 0.006	0.003 0.002 0.008 0.008	0.002 0.004 0.006 0.006	0.008 0.013 0.001 0.001	0.029 0.036 0.004 0.008	0.088
e e	0.021	0.010	0.032 0.013 0.008 0.010	0.003 0.018 0.013 0.025	0.025 0.029 0.016 0.009	0.212 0.033 0.006 0.015 0.017	0.017
Cu	0.004 <0.001 0.004 <0.001	0.010 0.005 0.005	0.030 0.004 0.002 0.002	0.002 0.005 0.006 0.006	0.006 0.021 0.004 0.004	0.009 0.007 0.003 0.003	0.002
Site	- 10 m 4 m	6 8 9 10	13 13 15 17 17 17 17 17 17 17 17 17 17 17 17 17	16 17 18 19 20	21 22 23 24 25	26 27 28 30 30	32

\* Concentrations in milligrams per litre

TOC	18	7.7	13	56	17	16	22	17	1		- ;	13	27	16	86	25	15	16	16	62	9	<b>-</b>
Ortho- phosphate-P	<0.01	2.94	0.15	0.11	70.07	0.31	0.27	3.34	<0.01		-	0.00	1.08	0.28	0.20	0.63	1.22	1.45	0.13	0.14	0.12	0.07
NO3+NO2-N	6.11	2.54	0.15	0.14	0.37	5.00	9.76	2.56	2.30	0.60	1.14	0.23	3.12	0.26	0.76	0.67	0.17	0.16	0.20	0.18	0.07	0.25
N+1,-N	0.129	0.120	0.156	0.133	0.125	0.140	0.270	0.330	0.070	0.065	0.039	0.040	0.137	0,000	0.133	0.040	0.152	0.100	0.036	0.058	0.058	0.134
НВ	<0.0002	0.0005	0.0002	0.0003	0.0002	<0.0002		- 000	0.0003	<0.0002	_		-	0.0003	<0.0002				-	0.0002	0.0004	0.0002
Pb	0.012	0.002	0.004	0.005	0.005	<0.001	0.001	<0.001	0.005	0.007	0.003	0.001	<0.001	0.002	<0.001				-	0.008	0.052	0.018
Cd	0.0070	0.0053	0.0063	0.0057	0.0058	0.0170	0.0043	0.0020	0.0005	<0.0002	0,0002	<0.0002	0.0050	0.0013	0.0044	0,0024	0.0002	0.0004	0.0003	<0.0002	-	-
As	0.003	<0.056	990.0	0.073	0.079	0.046	0.062	0.056	<0.002	0.014	900.0	<0.002	0.075	<0.002	0.065	0.019	0.015	0.018	<0.002	0.003	0.013	0.008
Zn	0.017	0.005	0.018	0.014	0.004	0.040	0.019	0.014	0.014	0.034	0.037	0.031	0.235	0.050	0.009	0.0013	1	0.020	0.019	ı—	-	-
Mn	0.061	0.012	0.011	600.0		-	0.013	0.118	0.004	0.004	<0.001	0.004	0.012	<0.001	0.012	0.016	0.013	0.010	0.001	0.002	0.001	0.003
F. O	0.025	0.037	960.0	0.130	0.040	0.080	0.080	0.010	0.014	0.007	0.003	0.002	0.008	0.017	0,000	0.031	0.050	0.065	0.012	0.002	0.002	900.0
Cu	0.003	0.003	0.026	0.022	0.022	0.011	0.026	0.048	0.003	0.002	0.003	0.003	0.015	0.003	0.010	0.002	900.0	0.010	0.001	<0.001		-
Site	7	a m	7	2	91	- 80	10	11	13	14	16	18	19	21	22	57	25	26	28	30	31	32

\* Concentrations in milligrams per litre

Table A4

Concentrations of Chemical Constituents in the Standard Elutriate\*

TOC	9	10	16	00	2	9	CV (	ω (	18	11	12	1	16	75	84	12	7	10	12	14	13	7	8	10	80	18	8	1-	#	m	8 2	
Ortho- phosphate-P	0.072	0.250	1 3	0.120	0.090	0.070	0,040	0.180	0.180	0,040	0,040	1				•	0.020	0.030	0,160	0.160	0.030				0.200	0.200	0.200	0.005			-	
NH14-N	0.42	1.00	4.50	1.20	0.63	96.0	96.0	3.10	6.50	04.4	4.00	1	3.80	5.10	2.00	3.40	3.00	06.0	1.60	1.60	3.50	6.20	5.70	0.33	15.60	31.20	13.20	0.01	0.01		-	
НВ	0.0020	0.0012	0.0019	0.0021	0.0014	0.0018	0,000,0	0.0009	0.0063	0.0036	0.0009	1	0.0056	0.0079	0900.0	0.0063	0.0022	0.0026	0.0001	0.0002	0.0004	0.0003	0.0003	0.0001	0.0045	0.0050	0.0100	0.0053	0.0075	0.0088	0.0050	
Pb	0.010	0.003	0.001	0.015	0.001	0.001	0.013	0.001	0.001	0.018	0.001	1	0.003	0.030	0.001	0.001	090.0	0.001	0.005	0.001	0.068	0.016	0.019	0.037	0.010	0.010	0.059	0.008	0.005	0.003	0.005	
Cd	0,000,0	0.0002	0.0001	0.0040	0.0004	0.0002	0,000,0	0.0004	0.0005	0,000,0	0.0001	1	0.0001	0.0017	0.0001	0.0001	0.0020	0.0002	0.0080	0.0005	0.0010	0.0050		•	-	0,000,0	0.0050	0.0020	0,000,0		-	
As	0.030	0.001	0.001	0.070	0.001	0.001	090.0	0.001	0.001	0.005	0.001	!	0.005	0.041	0.004	0.005	0.030	0.001	0.081	0.012	0.036	0.065	0.036	0.033	0.049	0.050	0.070	0.030	0.050	0.050	0.070	
Zn	0.004	0.660	0.056	0.014	!	0.003	0.004	!	!	0.003	1	1	0.024	940.0	0.014	0.055	0.038	0.029	0.004	1	0.065	0.007	0.010	0.030	900.0	0.026	0.007	0.023	0.008	0.004	0.009	
Mn	0.04	0.02	0.32	0.23	0.48	2.16	0.02	1.73	1.27	0.23	19.0	1	1.10	2.33	0.78	0.45	0.65	0.59	19.0	0.72	70.0	2.88	3.35	00.00	14.10	47.0	0.8%	0.01	0.02	0.03	0.01	
F.	0.03	2.48	0.24	1 8	0.07	90.0	0.02	69.0	60.0	١	0.08	1	0.17	0.51	0.19	40.0	0.30	0.52	0.05	90.0	0.36	1	90.0	0.02	0.02	40.0	40.0	0.17	0.17	0.15	0.16	
Ca	0.011	0.008	900.0	0.005	600.0	900.0	0.005	900.0	0.009	0.004	0.012	!	0.003	0.005	0.004	0.026	400.0	0.014	0.007	0.014	0.011	0.003	0.036	0.002	0.011	0.003	0.003	0.004	0.004	0.003	0.005	
Site	1	CU	m_	<b>4</b> 1	2	9	_	ω	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	54	25	56	27	28	53	30	32	

\* Concentrations in milligrams per litre.

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Brannon, James M

Long-term release of contaminants from dredged material / by James M. Brannon, Russell H. Plumb, Jr., and Issac Smith. Vicksburg, Miss.: U. S. Waterways Experiment Station; Springfield, Va.: available from National Technical Information Service, 1978.

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